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Process Modifications for Improved Carbon Fiber Composites: Alleviation of the Electrical Hazards Problem

Kumar Ramohalli

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FOREWORD

This report presents the results from a study covering the period June 1978 - May 1980, by the Chemical and Biological Processes Section at the Jet Propulsion Laboratory, California Institute of Technology. Contributors included Kumar Ramohalli, Warren Dowler, Robert Gauldin, Carol Glazer, Jan Harper, Marshall Humphrey, Glen Hull, William Mueller, Dennis O'Connor, Fred Tervet, Giulio Varsi, Lien Yang and Elizabeth Yen.

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ABSTRACT

This report describes attempts to alleviate through fiber gasification carbon-fiber-composite electrical hazards during airplane-crash fires. Thermogravimetric (TGA) and differential scanning calorimetric (DSC) experiments found several catalysts that caused fibers to combust when composites were exposed to test fires. An important synergistic effect among catalysts was also demonstrated.

State-of-the-art and modified composites were tested in the "Burn-Bang" apparatus developed by Ames Research Center, and in a high-voltage electrical detection grid apparatus developed by JPL. In a standard three-minute burn test the modified composites released no fibers, while the state-of-the-art composites released several hundred fiber fragments.

Techniques were pursued to decrease the approximately 10% mechanical-property deterioration accompanying catalytic treatment. Additionally, studies compared expected service life with and without catalytic modification, and electron microscopy and X-ray microanalysis furnished physical-appearance and chemical-composition data. Furthermore, an acrylic acid polymer fiber coating was developed that wet the carbon fiber (T300) surface

uniformly with the catalyst, providing a marked contrast with the uneven coats obtained by solution-dipping. Also, studies at Pennsylvania State University yielded important data.

Several promising new concepts resulted from the project, including catalytic elimination of carbon particulates from Diesel exhaust, catalytic improvement of coal combustion, and electrical destruction of carbon particulates in combustion systems in general.

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I. INTRODUCTION

Carbon fiber composites are envisioned to be used in increasing quantities in the future. These applications range from aerospace structures to consumer goods. It was of interest to alleviate the possible electrical hazards (Ref. 1-3) associated with such composites. The potential electrical hazard itself is considered beyond the scope of this effort and thus will not be discussed in this report. For information on the risks involved, reference can be made to proceedings of meetings explicitly devoted to that topic (Refs. 4, 5). However, throughout this work it was the aim to specifically prevent the release of electrically conductive carbon fiber fragments when the composite is exposed to an aircraft crash-fire scenario. More specifically, it was the objective of this project to prevent the release of carbon fiber fragments by gasifying the fibers, and various other possible solutions were specifically excluded from consideration during the performance of this project. In addition to electrical hazard alleviation through gasification, the project enabled involvement in the field of reactivity of carbon in air and in air combined with matrix pyrolysis and combustion products. This is an interesting and challenging field that has been studied over many years because of the innumerable important applications in various branches of science and technology.

This report is structured to present the data from several subtasks that comprised the effort. A systematic search was conducted for catalysts within the general framework of gasifying the fibers by means of a small modification to the state-of-the-art carbon fiber composites. A literature search was not

an aim of this project. The nature of the project was influenced to a large extent by the nature of the requirements. Chronologically, a one-month effort was initiated in March 1978 to suggest possible catalysts which could aid the gasification of the carbon fibers. At the end of the one-month feasibility study, which identified many avenues towards a solution (Ref. 6), a four-month effort was initiated in June 1978 to specifically explore the gasification scheme. Here the explicitly stated objective was to find catalysts for gasification. After this was successfully demonstrated in August 1978, a one-year project was initiated in October 1978 to find methods of including the catalysts in the composites and to study the effects of the catalyst on the properties of interest in composites. These are typically epoxy polymer matrix compatibility, mechanical properties, aging characteristics and of course the electrical hazards due to fiber release in an aircraft crash-fire situation. This history of sponsorship has a bearing on the work described in, and the structure of, this report.

Three representative carbon fibers were acquired: Thornel T-300 (Union Carbide), Magnamite AS-4 (Hercules) and the Pitch Fiber P (Union Carbide). These were tested in the thermogravimetric analyzer up to 1000°C under the different atmospheres of air, nitrogen and helium for weight loss rate measurements. The heating rates were varied. Many isothermal runs were also conducted. Concurrently, differential scanning calorimetric tests were run on the same fibers to determine their reactivity up to 500°C. These tests were repeated with

the catalyst treatment on the fibers In addition to these, a few experiments were conducted to pursue the novel approach of gasification through hydrogenation of the carbon fiber surface. Here the aim was to explore the possibility of combining hydrogen with carbon in order to pyrolyze and thus gasify the fibers. The hydrogen inclusion scheme was only briefly explored and was discontinued in the light of the proven success of the oxidative catalysts used in most of this work.

A contract was awarded to Professor Philip Walker, Jr. of Pennsylvania State University to draw upon the vast store of knowledge at the University on the characterization of the reactivity of carbon. Here the aim was to find fundamental mechanisms for the enhancement of the reactivity of carbon fibers in air. This report includes as an appendix the contribution from this fundamental study. The effect of the catalysts found at JPL was borne out by these tests also.

The catalysts found to be most effective are the weak acid salts of Group II metals. Also an important synergistic effect was found among some of the catalysts. The data from DSC on activated carbon particles show that the combination of catalysts produces larger exotherms than the individual catalysts. This aspect needs to be studied further with the specific intention of optimizing the catalyst selection.

The catalyst inclusion in the composite was studied in some detail. One of the important problems is the nonwettability

of the carbon fiber surface with most catalyst solutions. While a simple solution-dip treatment produced gasification, the coat was so non-uniform that obvious questions arose regarding the possible effects on the integrity and mechanical properties of the composite. One of the materials wetting the carbon surface was found to be an acrylic acid polymer. Hence, from a consideration of the surface free-energies and the catalytic ion (or ions, which were to be chemically included in an acrylic acid polymer), a technique was investigated for incorporating the catalyst into a surface-sizing material. This water soluble acrylic acid polymer was surface coated on the fiber, dried and then cross-linked with the catalytic ions when they were applied from solution to the fibers. This treatment resulted in a uniform dispersion of the catalyst on the fibers. The uniformity is demonstrated through a comparison of the scanning electron microscope photographs of solution dipped fibers.

The state-of-the-art and the modified composites were tested for possible fiber fragment release in a typical crash-fire situation. The "Burn-Bang" apparatus developed by the NASA Ames Research Center and the high voltage grid counter developed by JPL for Langley Research Center (LaRC) were used. The former collects the fiber fragments on a net for subsequent counting while the latter makes an in situ count. The fiber fragments collected in the Ames apparatus are available for comparative analyses. The lack of fiber counts in the JPL/LaRC apparatus clearly demonstrated that hardly any fiber fragments are released by the catalytically modified composites; in contrast, many fiber fragments are counted in the case of the state-of-the-art composite.

The mechanical properties are studied following the most widely employed tests. Here the aims are twofold: first to ascertain that the composites processed at JPL are indeed satisfactory in comparison with those at the various other processing centers including industry; second, to determine the effect of the catalyst modifications on the mechanical properties. The ASTM short beam shear test is used extensively as an index of the mechanical properties associated with the bond between the fiber and the matrix. In addition, a few tests are also conducted in the ASTM-recommended four point flexure. The mechanical properties of the JPL processed state-of-the-art composites are comparable to those processed elsewhere (other NASA centers and industry). With the chemical modification for catalytic gasification, the mechanical properties show approximately 10% deterioration. This aspect needs to be studied further.

The important question of service life is pursued in the state-of-the-art and the modified composites. Here the aim is to determine the extent of alteration of the useful service life of a composite when modified for the alleviation of the electrical hazards. The composites are "aged" in an accelerated manner in a predetermined program of elevated temperature storage under stress for specified lengths of time. The variations in the mechanical properties with the accelerated "age" give an indication of the expected service life. Most important, these tests indicate the relative aging characteristics of the state-of-

the-art and modified composites. It is natural to expect that the useful service life of the composite would be reduced with the enhanced reactivity of the ingredients. However, the results so far do not show any deterioration in the predicted useful service life with the catalytic modification.

The results are summarized in the last section and the pertinent conclusions are drawn.

In the course of this investigation, because of the fundamental nature of these studies, several promising areas have been identified for further research. These are problems of national concern. In the general area of composites, the process modification of prestressing appears to hold promise for increased strength to weight ratio, more efficient use of the ingredients and a large deformation at failure. Preliminary results support this view. Also, the concept of hollow fibers emerged enabling greater use of the load bearing parts of the fiber - the outer shell rather than the inner core. Here the estimates show that the stiffness of a composite can be substantially improved (approximately 50%) for a given weight through the use of hollow fibers.

The enhancement of the reactivity of carbon has wide applications other than in the composites. One of them is the particulates exhaust problem acknowledged with the Diesel

engine automobile. There are indications that some form of catalytic combustion of these carbon particulates can alleviate the problem. With the general trend in the automobile industry towards more Diesels to achieve high fuel efficiencies, the area of catalysis of carbon particulates appears worthy of pursuit.

Coal combustion is also becoming very important with the dwindling oil supplies. Here the reactivities of coal in air are so low compared to the hydrocarbon oils that large furnaces are needed for a given throughput. Again, the catalytic enhancement of the coal reactivity can greatly increase the throughput for a given size, or reduce the size for a required throughput. An important application appears to be in the areas of ash and slag fouling. Chemicals were found in this investigation that significantly alter the melting points of some intermediate products in the combustion of carbon fibers. When transformed to coal combustion, the possibility arises that the ash and slag melting point can be significantly altered so that these can be simply removed without shutting down the plants for ash and slag cleanup. The cost savings can be considerable.

II. AVAILABLE LITERATURE AND CONTACTS

An exhaustive literature search was not one of the aims of this study. Within the time constraints the choice was made to contact some of the leading authorities in the field of carbon and graphite oxidation and combustion, in particular, and more generally the experts in the field of combustion. The requirements of carbon fiber gasification were brought up during some meetings of The Combustion Institute. Several university professors and researchers in industry were also contacted. A quick literature search was also conducted using a JPL computer search of several data bases.

Many interesting, and indeed, useful items emerged as a result of the above attempts. It was discovered, for example, that sodium and potassium are good catalysts in the reactions of carbon (Reference 7). It was found that graphite is very difficult to oxidize because of its stable structure. Nevertheless, it has been reported that silver, vanadium and vanadium pentoxide are very powerful catalysts (References 8 and 9) having the capability even to open up the basal plane of graphite. Carbon oxidation and combustion have also shown the effect of many salts. Voluminous data are available on various aspects of oxidation (Reference 11). (Please see the excellent series "Chemistry and Physics of Carbon," Philip Walker, General Editor, Marcel Dekker Publishers, Vols. 1-14.)

While the above exercise was useful and indeed informative, no catalyst appeared to be readily available to serve our specific need of gasifying, through combustion, the carbon fibers used in composites. Krylov (Reference 10) has laid down some basic criteria that may be helpful in selecting catalysts. He points out, based on a theory of electron transfer, that metals with first work function* less than 4.3 eV ought to be good catalysts in the oxidation of carbon. The periodic table with the elements (as oxides) that meet this criterion is shown in Figure 1. It can be seen that the following elements are expected or implied to be able to catalyze the oxidation of carbon: Ca, Na, K, Cs, Mg and Ba.

In spite of all of this information it appeared fairly certain that no catalysts have been reported to induce the self-sustained combustion in air of carbon fibers in the absence of an external heat source. This belief is further reinforced by the fact that no reports on this specific task surfaced during the extensive literature search that went into the application for a patent disclosure (Reference 12) following the discovery of powerful catalysts at JPL.

* Energy needed for removing the first orbital electron from the atom.

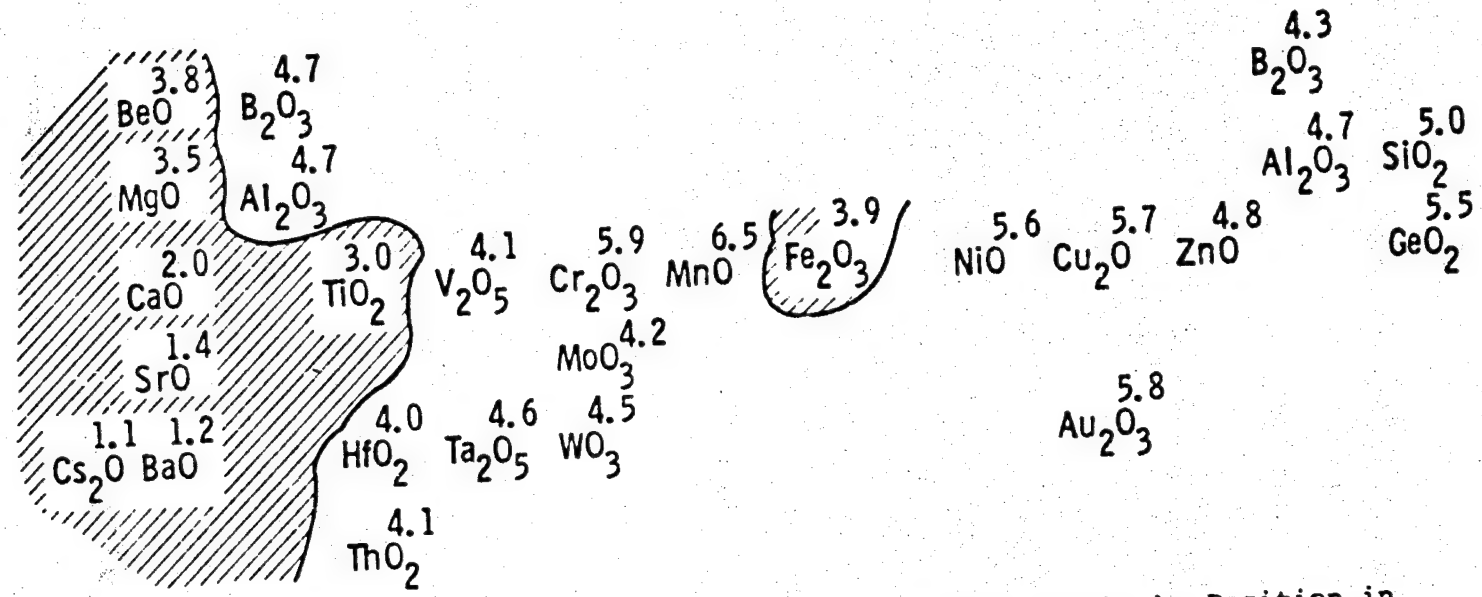

Fig. 1. The Relation Between Work Function of Oxides With the Position in the Periodic Table of the Metal Forming the Oxide.; Crosshatched Oxides Have a Value of $\phi < 4.3$ eV. (Source: Krylov, Reference 10)

III. THE SELECTION OF CATALYSTS

Some of the early attempts at the catalyst search and the test results have already been reported (Reference 6). The selection of the catalyst is influenced by the criterion used to prove its effectiveness upon ignition. *Self-sustained combustion of graphitic carbon in air in the absence of an external heat source was used as a primary criterion in catalyst selection.* The residue after combustion is required to be free of carbon (see Table I). The catalyst application technique received some attention early in the program. Fine dispersion was thought to be essential. However, some of the results show surprising insensitivity to the fineness of catalyst dispersion on the fibers. The tests were conducted in the TGA and in the DSC on the fibers as received and after the treatment. The following four methods were used to deposit the catalyst on the fibers: Solution dip, solution boil, vapor deposit and electrical sputtering. A brief description of each of these follows:

(i) Solution Dip. Aqueous solutions of the salts consisting of 1%-10% salt were prepared. After solution dip, the fibers were air dried to constant weight.

(ii) Solution Boil. This was essentially what the name implies. The fibers were boiled in a solution of the catalyst salt for ten minutes and the liquid decanted away. The fibers were then air dried to constant weight.

TABLE I: Determination of Ash Following Burning of Carbon Fibers

Treatment	Mass of Fiber	Mass of Treatment	% Treatment	Mass of Ashes	% Ash
1% Calcium Acetate Solution Dip	45.8	0.1	0.2	8.7	19.*
	82.5	0.3	0.4	13.8	17.*
	66.3	1.0	1.5	4.2	6.2*
	99.2	1.5	1.5	6.7	6.6*
3% Calcium Acetate Solution Dip	63.8	1.2	1.8	1.3	2.0
	55.8	1.4	2.4	1.4	2.4
10% Calcium Acetate Solution	152.7	13.5	8.1	7.5	4.5
	44.9	5.0	10.0	1.9	3.8
	90.8	5.8	6.0	2.7	2.8
10% Solution of 75:25 mix of Lithium and Calcium Acetate	74.2	8.2	10.0	5.3	6.4
	61.8	4.9	7.3	3.3	4.9
	48.0	3.2	6.2	3.3	6.4

* Fibers found in residue

(iii) Vapor Deposition. Thin films (0.01 μm to 1 μm) of catalytic material were deposited on the fibers by evaporation in a vacuum ($<10^{-4}$ Pa) using the apparatus shown in Figure 2a. The material to be deposited was heated to the point of evaporation by being placed in an electrical resistance heating element in the form of either a wire basket or a metal "boat". The vapor from the heated material was deposited on the fibers. Since the vapor travels in a nearly straight line, the fibers were rotated in the vapor so that a uniform coating was acquired.

(iv) DC Electrical Sputtering. A film of the catalytic material can be deposited on the fibers by a direct current sputtering technique (Figure 2b). Both the material to be deposited and the carbon fiber sample to be coated were placed in a 1 KV dc plasma of argon ions. The material to be sputtered was used as the cathode and the specimen was placed on the anode. Material eroded (sputtered) from the cathode by the ions of the plasma are deposited on the sample of carbon fibers. Because of the multiple scattering in the plasma, sputtering produced a fairly uniform coating and the individual fibers in a bundle without the need to rotate the specimen during coating or to completely separate the individual fibers from each other.

Etching: The nonwettability of the carbon surface of the fiber was recognized early as an important problem. A ten minute exposure to an argon plasma (Figure 2c) greatly improved the wettability. This improvement is shown in Figures 2d and 2e where the coating on the fibers is one of the early

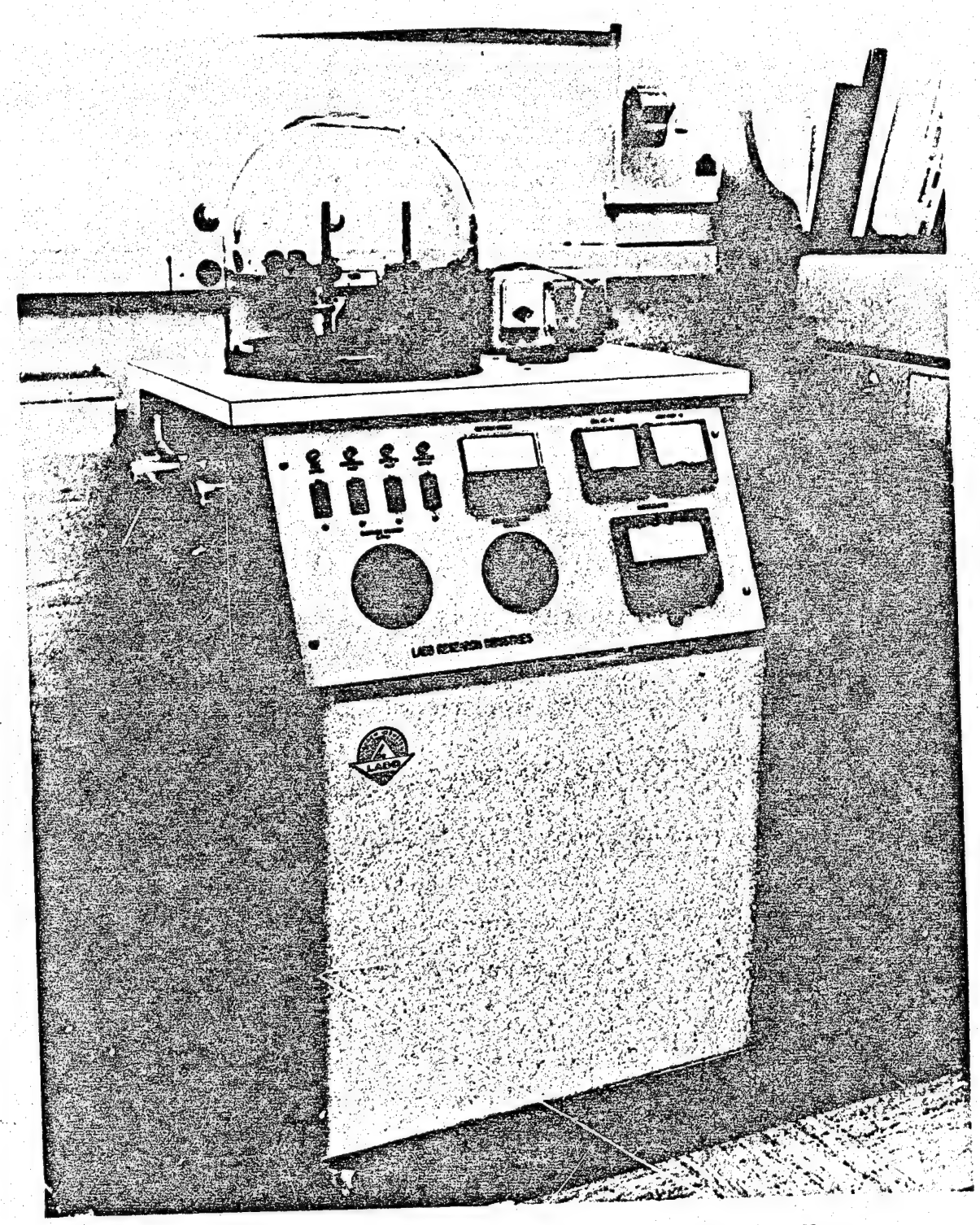

Fig. 2a. The Ladd Vacuum Evaporator Used for Vapor Deposition of the Coatings on the Fibers

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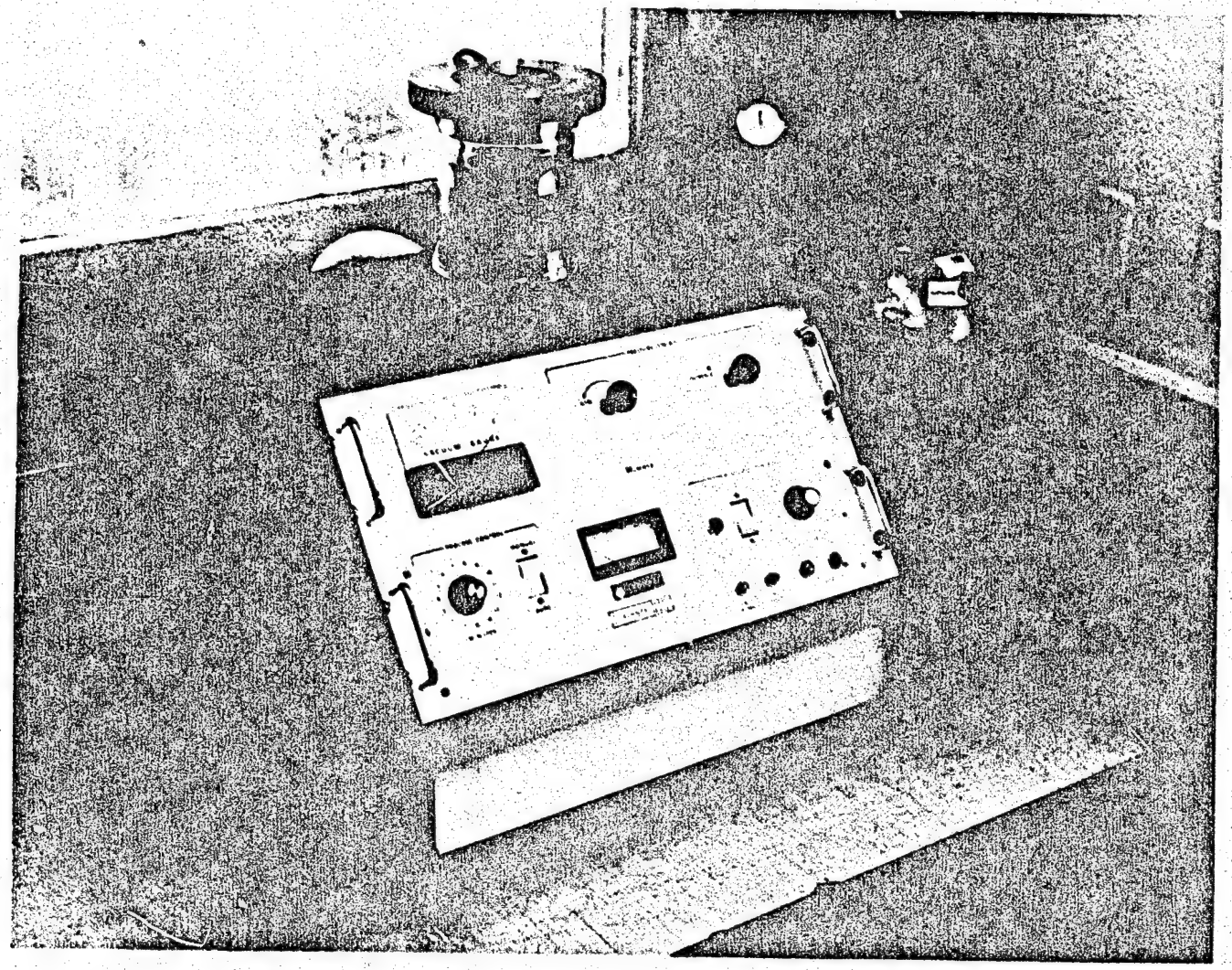

Fig. 2b. The D.C. Electrical Sputtering Apparatus Used in Some of the Coatings

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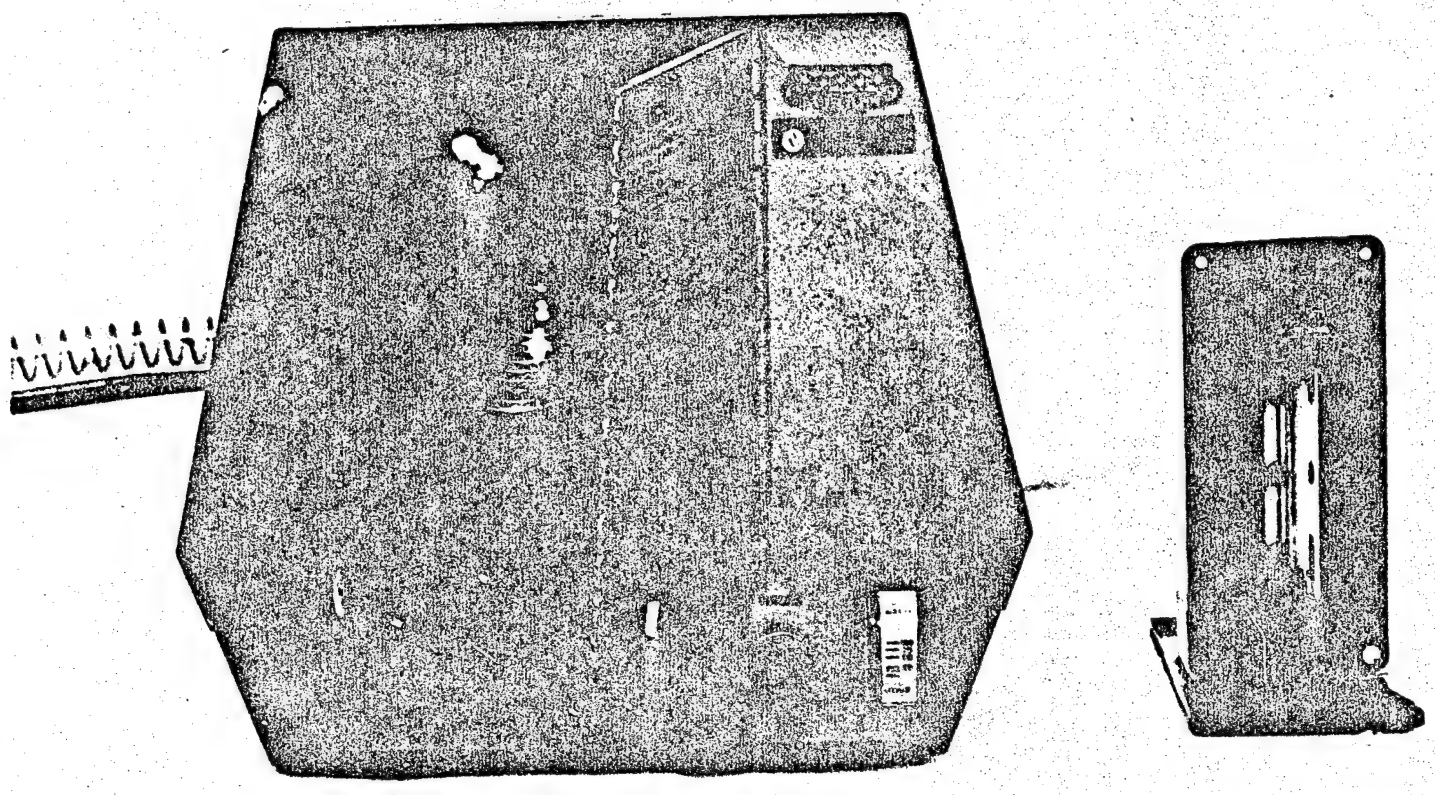

Fig. 2c. The Plasmod Plasma Source Apparatus for Etching the Fibers

Fig. 2d. The Wettability of As-Received Thornel-300 Fibers as Seen with a Coating of EC + TCP from a Solution in Acetone with Solution-Dip of the Fibers.

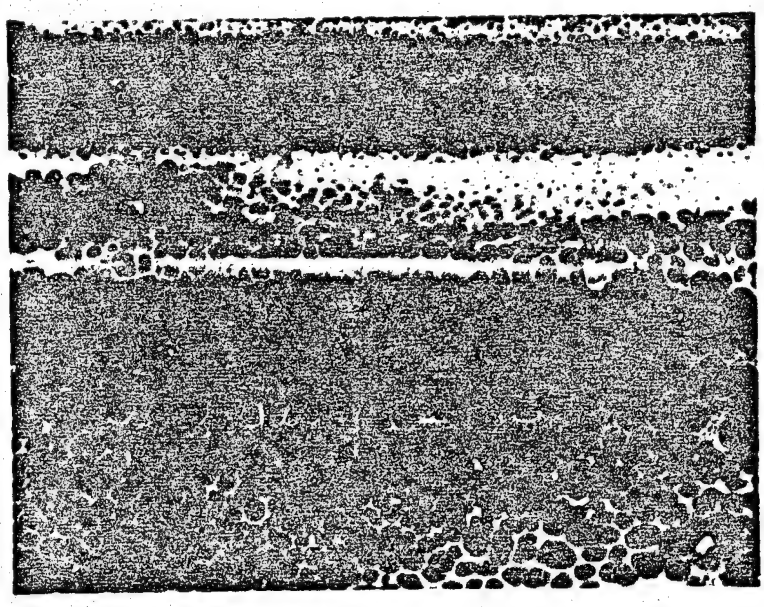

Fig. 2e. The Wettability of Argon Plasma Exposed (etched) Thornel-300 Fibers as Seen with the Same Coating of the Same Chemical Solution (EC + TCP) shown in Fig. 2d above.

candidates which was not used subsequently. The point should be clear, however, that an argon plasma can vastly improve the wettability of carbon fibers. A mechanism has since been suggested by Professor P. L. Walker that the argon plasma creates sites for oxygen attachment upon subsequent exposure to air. The general subject of surface wettability has been understood in terms of surface free energies.

The DSC and TGA Tests

Several hundred runs were made in the DSC (Figure 2f) and TGA (Figure 2g) apparatuses to determine the relative behavior of the fibers with and without the catalytic treatment. Some of the raw traces are shown in Figures 3 - 6. Most of the runs were conducted in air. Some were conducted in an atmosphere of nitrogen. For comparison with the latter (to determine the possible reactions of carbon with nitrogen, in presence of moisture) a few runs were conducted in an argon atmosphere. One of the most interesting runs was the TGA run in air where water vapor was introduced into the nitrogen purge stream. This saturation level of moisture showed a remarkable effect in essentially consuming a good portion of the fibers (Figure 7).

There are various ways in which the TGA and DSC data can be interpreted. The data were fitted to an Arrhenius plot, assuming a first-order reaction. The results showed unacceptable inconsistencies depending upon the heating rates and the extent of reaction. It was felt that the actual chemical reaction schemes may be sufficiently complicated to preclude such a simple interpretation. Such a feeling was

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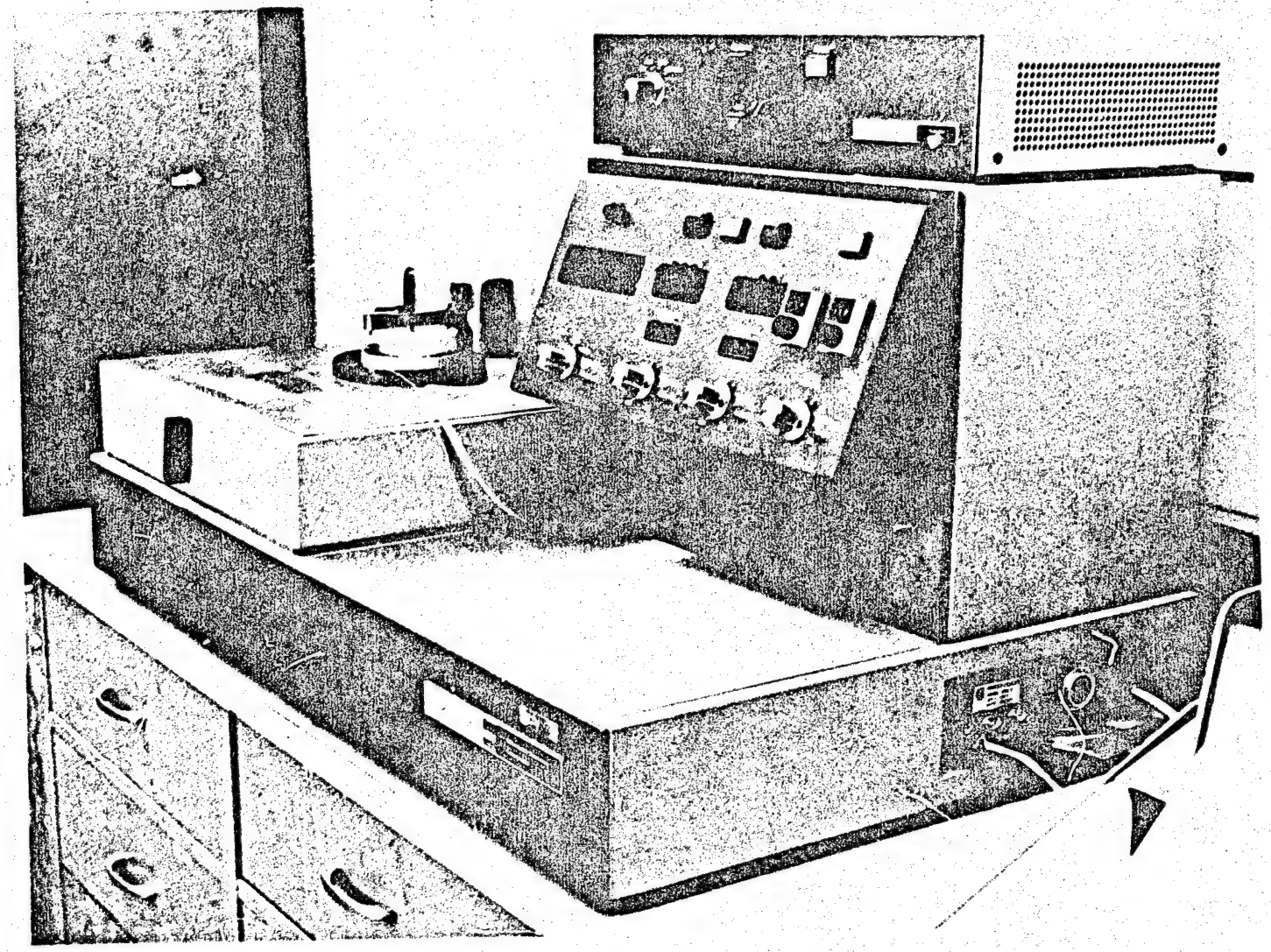

Fig. 2f. The Perkin-Elmer Differential Scanning Calorimeter Used in the Determination of the Exo- and Endothermic Reactions of the Treated Fibers.

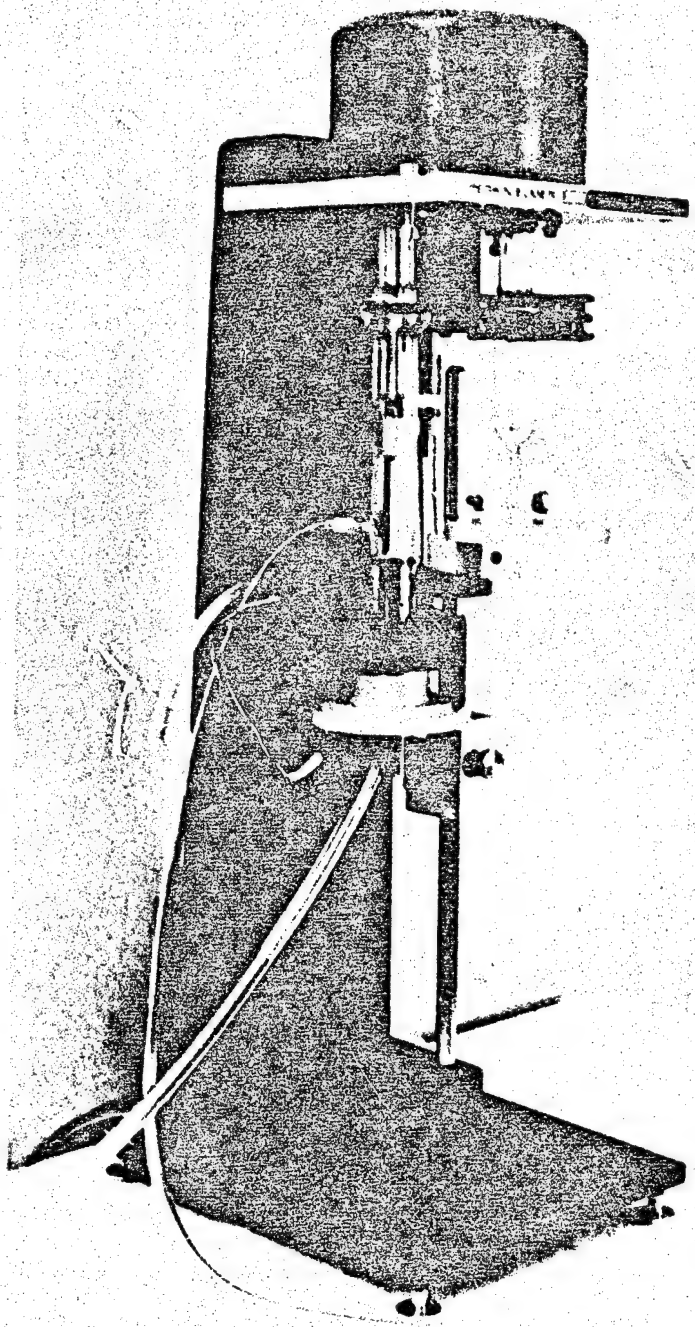

Fig. 2g. The Perkin-Elmer TGS-2, Thermogravimetric Analyzer Which Has the Provision for Varied Heating Rates and the Atmosphere of the Test.

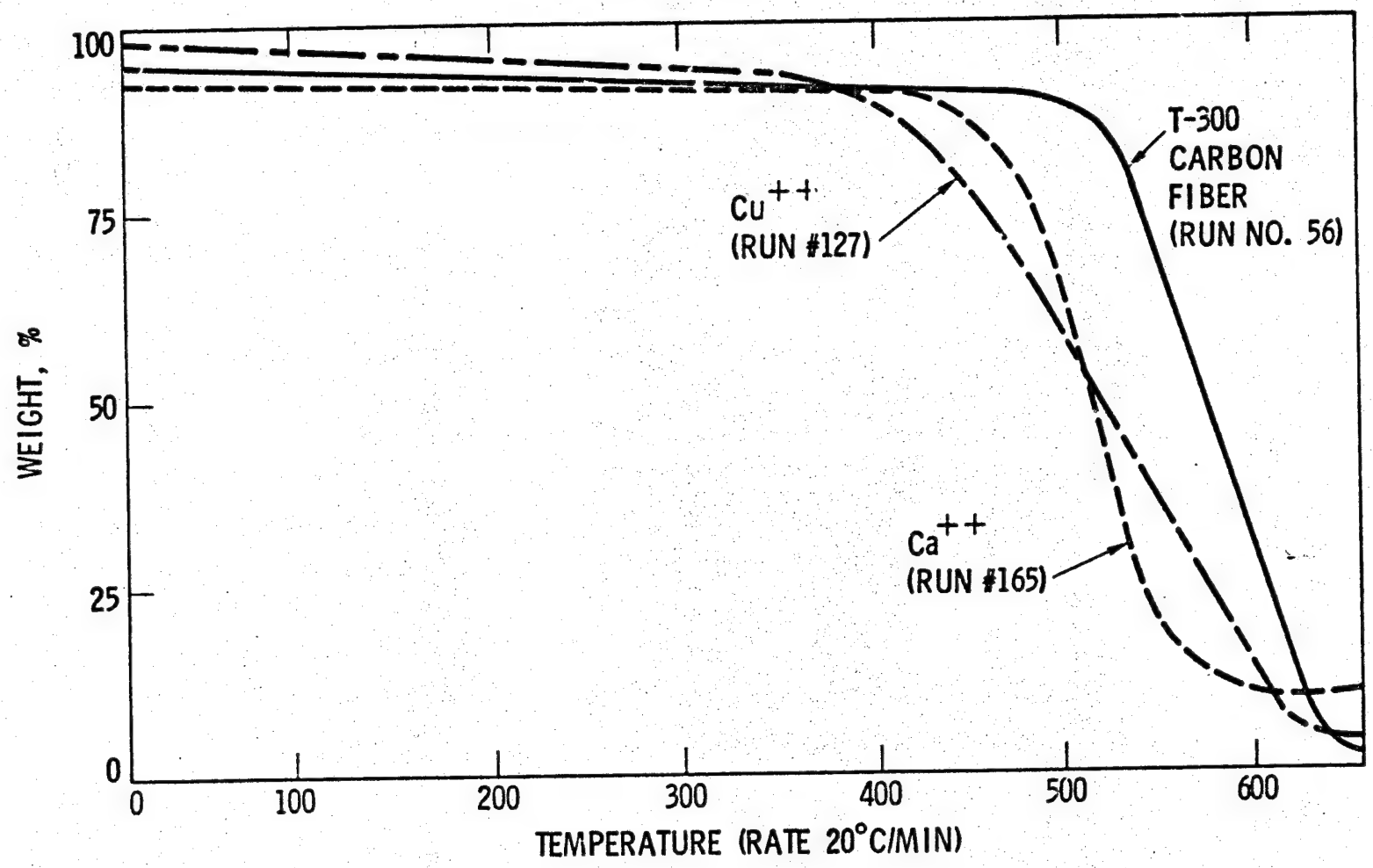

Fig. 3. TGA Traces of Carbon Fibers

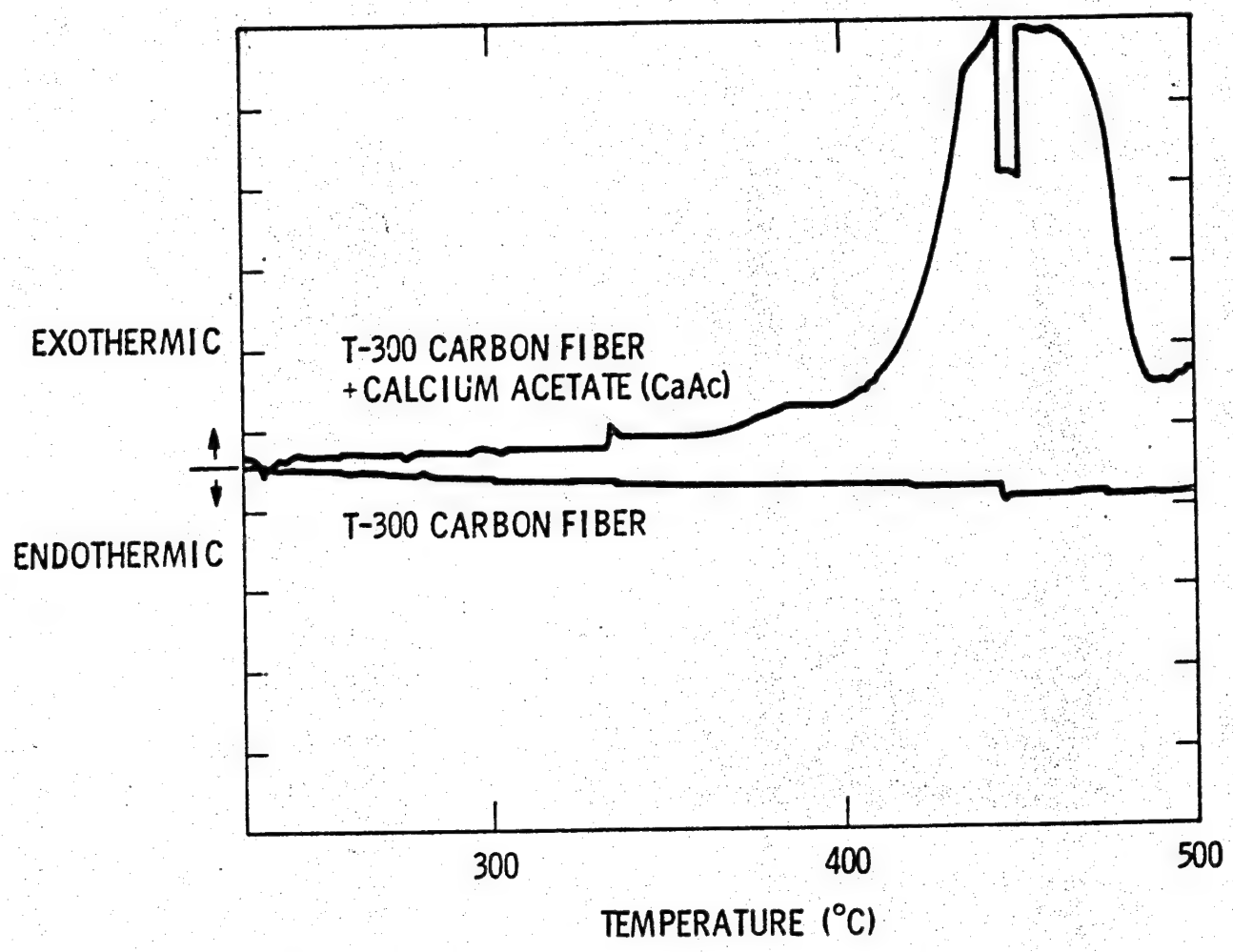

Fig. 4. DSC Traces of Treated and Untreated Carbon Fibers in Air.

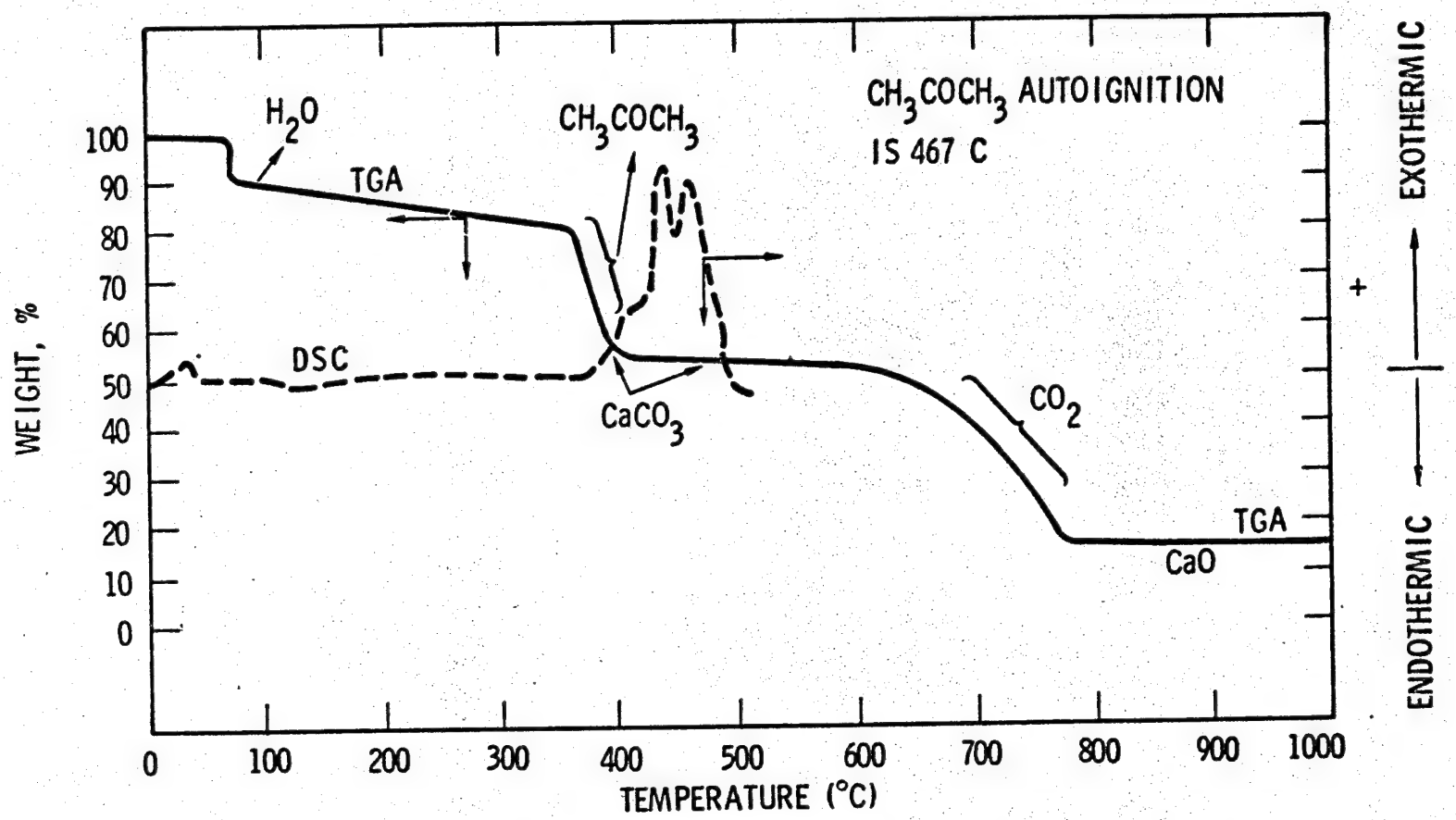

Fig. 5. A Comparison of TGA and DSC Traces for Neat Calcium Acetate. The liberation of acetone around 360 - 380°C results in significant weight loss in the TGA. This acetone reacts exothermically in air around 467°C resulting in the exothermic peaks seen around 450 - 480°C.

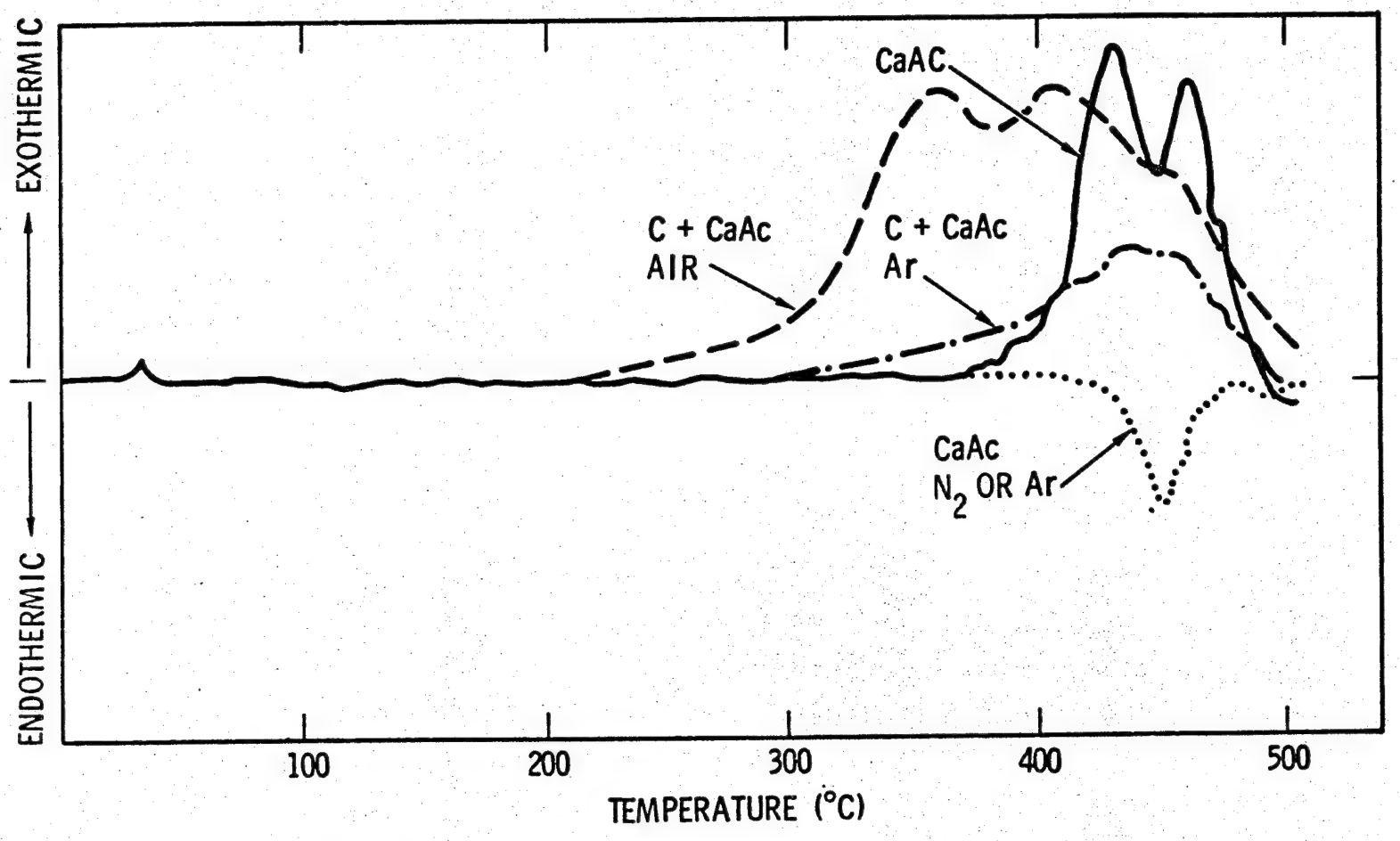

Fig. 6. DSC Traces of Calcium Acetate Treated Carbon Samples in Various Atmospheres at a Heating Rate of 20°C/min.

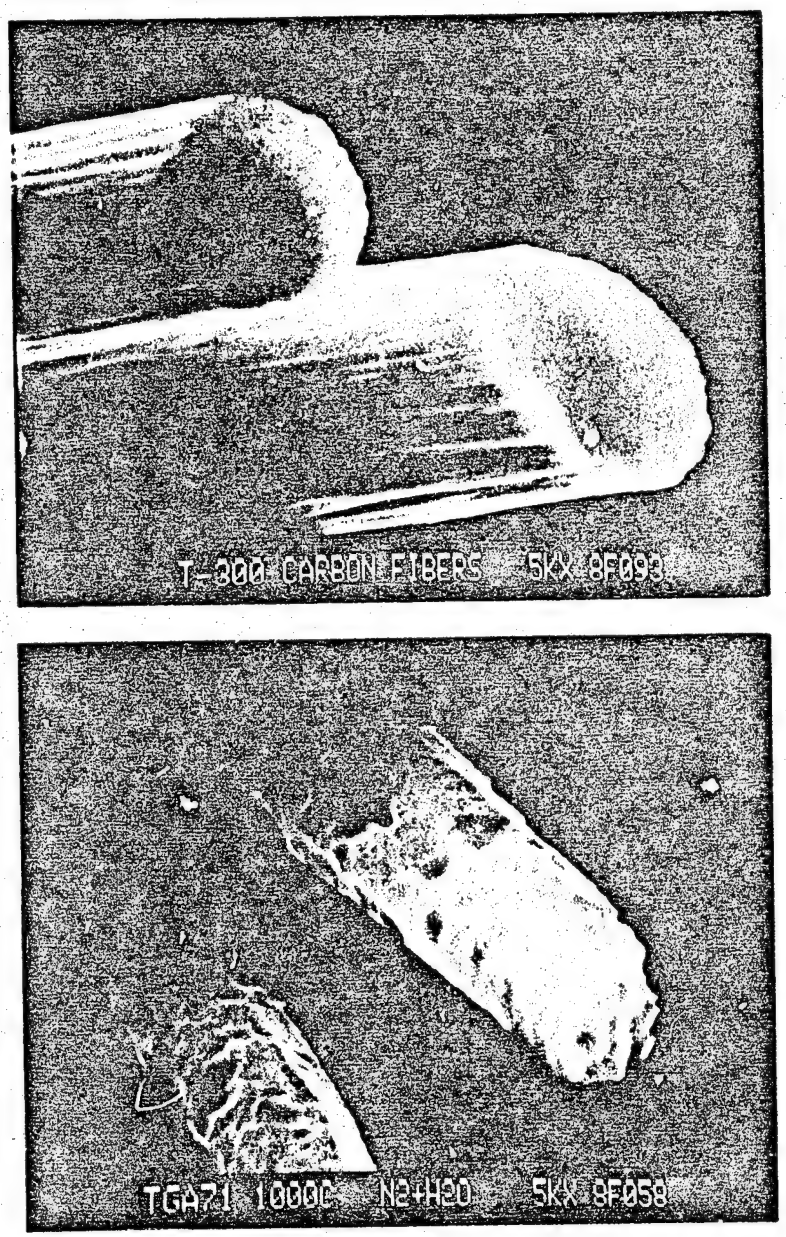

Fig. 7. SEM Photographs Showing the Effect of Water Vapor in the Atmosphere in the High Temperature Behaviour of the Fibers. As-Received Fibers are at the Top; Fibers after Exposure to Air Saturated with Water Vapor at 1000°C for a Brief Duration are Shown at the Bottom.

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subsequently borne out at a meeting where several leading experts in the field of carbon combustion, Professors P. L. Walker and G. Gavalas, shared their vast experiences with us. The fact emerged that the reactions in air of carbon in the form of fibers and coal (i.e., less than 100% carbon content) can be most complex and have defied adequate description.

Under the circumstances, the data are interpreted in the following manner. The temperature at which some prominent reactions become apparent is identified as the "action" temperature. Typically, this is the temperature at which the slope is a maximum in the weight versus time curve in the TGA. Also the temperature (time) interval over which the weight of the sample changes from 90% to 10% is an indication of the rate of the reaction. This range is also computed for many runs. The residual weight at the final temperature, or alternatively, the time for constant weight to be reached is also an indication of the reactivity. In the DSC runs, the extent of exothermic reaction as indicated by the value at the peak gives some indication of the reactivity.

While absolute predictive information may be somewhat difficult to extract from such interpretations, relative information is easily extracted. For the catalyst treatment, since relative information is all that matters, Tables II, III and IV have meaningful information on effectiveness. The following discussions result from these tables.

Table II: TGA Data of Carbon Fibers*
Non-Isothermal Runs

Fiber and Treatment	Initial Weight (mg)	Final Weight (mg)	Purge Gas	% Weight Loss	T (C)
Perkin Elmer (Model No. TGS-1)					
AS-4	0.979	0	Air	10 50 90	480 565 625
T-300 CaAc	0.816	0	Air	10 50 90	505 555 595
T-300 10% CaAc	0.85	0.01	Air	10 50 90	530 560 595
T-300 10% Li-CaAc	0.933	0.04	Air	10 50 90	520 630 700
DARCO - G60 +BaAc	0.910	0.5	Air	10	360
Ca Acrylate	0.791	0.228	Air	10 50	200 610
Ca Acrylate	0.858	0.267	Air	10 50	330 650
T-300	0.965	0	Air	10 50 90	460 555 615
T-300	0.695	0	Air	10 50 90	480 580 630
T-300	2.730	2.358	N_2	10	910
T-300	2.578	2.22	N_2	10	880
T-300	0.478	0	N_2	10 50 90	490 585 655

*The abbreviation Ac stands for Acetate, throughout this report.

Table II: TGA Data of Carbon Fibers
Non-Isothermal Runs (Continued)

Fiber and Treatment	Initial Weight (mg)	Final Weight (mg)	Purge Gas	% Weight Loss	T (C)
Carbon Fiber	2.610	0.003	Air	10 50 90	530 600 640
Carbon Fiber	2.782	1.915	Air	10	705
T-300	0.932	0	Air	10 50 90	500 555 605
T-300	0.940	0.029	Air	10 50 90	500 575 615
T-300	0.845	0	Air	10 50 90	500 575 620
AS-4	0.611	0.456	N_2	10 25	710 1000
AS-4	0.985	0	Air	10 50 90	505 590 650
Hydrogenated Fibers with Pd-Ag. All the samples were T-300 with 75% Pd, 25% Ag, H2 at 500 psi for 30 minutes	0.696	0.581	N_2	10 16.5	810 990
	0.758	0.570	N_2	10 24.8	710 980
	0.720	0.618	N_2	10 14.2	870 1000
Perkin Elmer (TGS-2 Model)					
T-300 Untreated	0.425	Not Recorded	Air	10 50 90	488 523 545
T-300 2% CaAc	0.828	Not Recorded	Air	10 50 90	505 545 580

Table II: TGA Data of Carbon Fibers
Non-Isothermal Runs (Continued)

Fiber and Treatment	Initial Weight (mg)	Final Weight (mg)	Purge Gas	% Weight Loss	T (C)
T-300 2% CaAc (wet)	0.868	Not Recorded	Air	10 50 90	560 590 625
T-300 2% BaAc	0.813	Not Recorded	Air	10 50 90	555 595 630
T-300 2% BaAc	0.930	Not Recorded	Air	10 50 90	585 620 645
T-300	0.932	Not Recorded	Air	10 50 90	635 665 695
T-300	0.830	Not Recorded	Air	10 50 90	620 655 690
T-300	0.697	Not Recorded	Air	10 50 90	620 655 690
T-300	0.675	Not Recorded	Air	10 50 90	640 670 695

TABLE III: TGA Data of Carbon Fibers

Isothermal Runs (Perkin Elmer TGS-2)

Fiber and Treatment	T_{iso} (C)	Average Time Min.	% Weight Loss
Pitch Fiber Untreated	700	20	50
Pitch - CaAc	700	3.5	50
Pitch - BaAc	700	9	50
T-300 Untreated	500	53	50
T-300 - CaAc	500	14	50
T-300 - BaAc	500	28	50
AS-4 Untreated	600	26	50
AS-4 - CaAc	600	12	50
AS-4 - BaAc	600	16.5	50

The purge gas was N_2 until the isothermal temperature, T_{iso}, was reached, then air was substituted.

Table IV: DSC Analysis of Carbon Fibers and Carbon Particles

Fiber and Treatment	Purge Gas	T (C) at Max Slope	T (C) at Peak Energy	ΔH at T_{peak} Relative Value from Baseline per mg
T-300 - 10% Scln Coated CaAc	Air	6 minutes at 500°C	6.25 minutes at 500°C	+55
T-300 - 50/50 CaAc	Air	420 450	432 457	+28 +35.5
T-300 - Untreated	Air			No Peak
T-300 50/50 CaAc		420 448	430 455	+22.7 +19.4
DARCO - 5% Li_2Co_3 95% CaAc	Ar	425	430	-5
DARCO Ca Acrylate	Air	475	485	+43

Synergism

From a point of view of optimum catalyst selection it is also of interest to determine the most effective combination of catalysts, and a quick attempt was made to determine synergism. Several solutions were made using mixtures of catalysts. For the purpose of simply investigating the synergistic effect on carbon reactivity, a more easily handled form of carbon was used; this was DARCO GLO, an activated carbon powder. The DSC plots are shown in Figure 8. The mixture of potassium and calcium acetates produces a far larger exotherm than either salt alone under otherwise identical conditions. This points to the possibility of employing smaller quantities of catalyst mixtures than what would be required if used on an individual basis.

Another form of synergism was also found to be valuable in these studies. On many occasions the need was felt for a material that holds the fibers together in a bundle while the catalytic combustion activity is in progress. Frequently, in an air stream, fiber fragments were seen to fly off and be quenched even while the primary catalyst was in the process of gasifying the fibers. Here the low melting point lithium compounds were examined as possibilities. A combination of calcium and lithium acetates was tried. It was found that lithium salts and products of combustion melt and hold the fibers together while the calcium salts complete the catalytic gasification. This was an important discovery and had a strong influence on

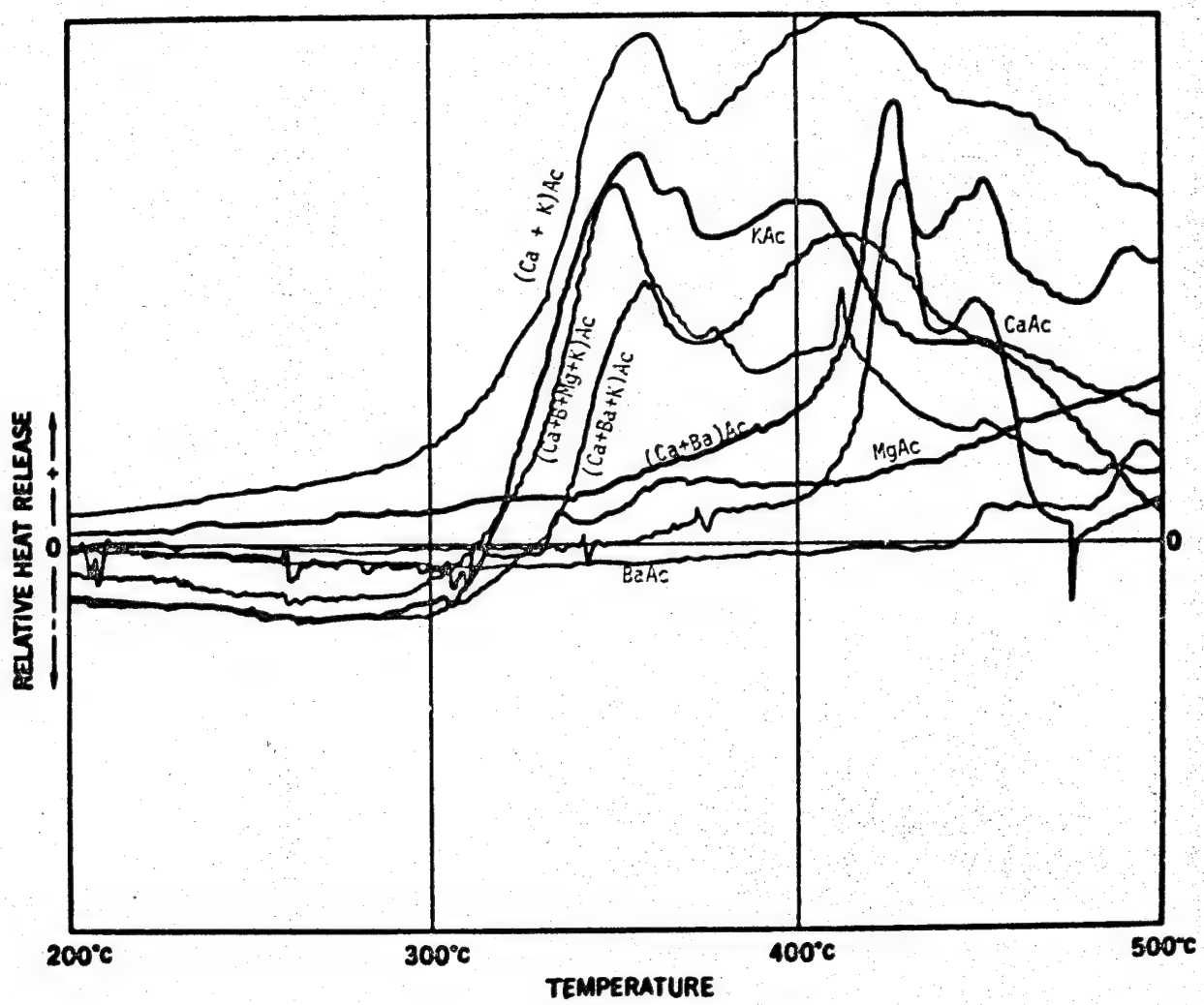

Fig. 8. DSC Data Showing Synergism. Note That (Ca+K)Ac is Better Than CaAc or KAc Alone. All of These Had 1% Treatment by Weight.

the subsequent tests. In fact, combinations of calcium and lithium acetates were almost routinely used in the tests since.

In the light of the earlier discussions on the complex nature of carbon reactions an attempt was made to fit Arrhenius kinetics to the oxidation of carbon fibers using the abundant TGA data. A few assumptions had to be made in order to apply the Arrhenius equation: (1) the partial pressure of oxygen above the graphite fiber surface remains constant through the reaction, (2) the surface area of the carbon fiber is proportional to the mass of the fiber, and (3) the proportionality constant is the same for all fibers of the same type.

Assumption (1) is valid provided that the mass of oxygen is much larger than that of carbon fiber, and the reaction rate is not so great that product gases create a large oxygen-concentration gradient near the fiber surface. Assumptions (2) and (3) could only be tested by seeing how well the data fit the Arrhenius equation derived below.

For a gas-solid reaction, the reaction rate can be given by

$$\frac{dm}{dt} = [O_2]S\ A \exp\left(-E_0/RT\right) \qquad (1)$$

where

A = Arrhenius pre-exponential factor

$[O_2]$ = Concentration of oxygen

E_o = Activation energy

m = Mass of carbon

R = Gas constant

S = Surface area of carbon

T = Reaction temperature

t = Time

From assumption (1) the oxygen concentration is constant. From assumption (2) and (3) the surface area of the carbon can be expressed as

$$S = m\,A_c$$

where

A_c is constant. Thus equation (1) reduces to

$$\frac{1}{m}\frac{dm}{dt} = K \exp\left(-E_o/RT\right) \qquad (2)$$

where K is a constant. However, data from the TGA experiment is in the form of mass change with temperature, not with time. The relationship

$$\frac{dm}{dt} = \left(\frac{dm}{dT}\right) \cdot \left(\frac{dT}{dt}\right)$$

is used with equation (2) to derive the final rate equation

$$\frac{1}{m}\frac{dm}{dT} = \frac{K}{(\frac{dT}{dt})} \exp(-E_o/RT) \qquad (3)$$

where $(\frac{dT}{dt})$ is the heating rate of the TGA apparatus.

In order to use equation (3), data from the TGA in the form of mass function of T_i was fitted to a polynominal ($m=\sum_{i=0}^{n} a_i T^i$) using a library program supplied with a Hewlett-Packard 9830A calculator. This program was enlarged to give the derivative of m with T

$$\frac{dm}{dT} = \sum_{i=1}^{n} i a_i T^{(i-1)},$$

and to then use this derivative to evaluate constants K and E_o from equation (3). This was done by taking the logarithm of both sides of equation (3)

$$\ln\left[\frac{1}{m}\frac{dm}{dT}\right] = \ln\left[\frac{K}{(\frac{dT}{dt})}\right] - E_o/RT$$

producing a linear equation of $\ln\left[\frac{1}{m}\frac{dm}{dT}\right]$ as a function of T^{-1}. The method of least squares was used to calculate the slope, $-E_o/R$, and the y-intercept, $\ln[K/(\frac{dT}{dt})]$. The values of E_o and K can then be determined.

Results are shown in Table V. The column headed by r is the correlation coefficient, which indicates the degree of

Table V: TGA Data for Arrhenius Equation Analysis

Run No.	Heating Rate (°C/min)	E_o	K	r
UNTREATED				
C1	1	67.4	8.39×10^{17}	0.987
C2	1	106.8	3.56×10^{28}	0.584
C3	1	64.1	9.79×10^{16}	0.974
C4	1	51.6	7.26×10^{12}	0.208
C5	20	45.6	9.50×10^{10}	0.988
C6	20	30.5	1.74×10^{7}	0.268
C7	20	49.5	8.17×10^{11}	0.928
C8	20	47.1	1.94×10^{11}	0.999
C9	5	48.1	5.47×10^{11}	0.9998
C10	20	44.9	5.69×10^{10}	0.844
TREATED WITH 10% Ba ACETATE SOLUTION				
A1	20	43.1	7.10×10^{10}	0.987
A2	20	42.9	1.02×10^{11}	0.960
A3	20	50.3	2.40×10^{13}	0.943
TREATED WITH 10% Ca ACETATE SOLUTION				
B1	20	50.0	9.69×10^{13}	0.331
B2	20	15.4	1.45×10^{4}	0.511
B3	20	20.2	1.67×10^{4}	0.224

agreement of the least squares fit. It should be noted that the agreement is generally very good (>0.9) or very poor (<0.55). All of the calcium acetate treated samples show very poor results, but for the other samples the poor degree of fit is random, perhaps the result of variations in surface area from sample to sample. Also, there is an increase in activation energy with heating rate. This phenomenon could not be explained. The general conclusion reached is that the assumptions made are faulty. In particular, the assumption that the surface area is directly proportional to the mass of the carbon fiber is too simplistic. If the combustion of the cylindrically shaped particles is uniform, the area would be proportional to the square root of the mass. Attempts to fit the data to an Arrhenius equation with this square root relationship resulted in lower activation energies, but with no improvement in correlation coefficients. A more reasonable model for the surface area would show the area increasing initially due to pitting of the solid, followed by a gradual decrease as the carbon is consumed. However, such a complicated model is beyond the scope of this research.

Ames Burn-Bang Box Tests

The Ames Box was developed by Mr. Richard Fish of the Ames Research Center, Mountain View, California for evaluating fiber release from burning composites. The test procedure consists of burning a rigidly mounted panel (13 cm x 1.3 cm x thickness) for three minutes, then striking the burned composite with an air-actuated "arrow." Ambient air is constantly drawn through

the box by a vacuum source. A nylon net treated with a tacky glue is placed in the exit line to the vacuum cleaner. This net will catch clumps of fibers or small pieces of composite, but individual fibers escape detection. Large pieces of composite remain in the box.

Tests of state-of-the-art and catalyst-treated composite samples revealed no significant differences in the number or size of composite pieces produced. This result was expected because the catalyst treatment creates only small changes in the mechanical properties of the composite. The anticipated result of the treatment, that is, a reduction in the number of individual fibers released, could not be measured by the box as it was supplied. In an attempt to count individual fibers, the net was replaced by the electrostatic grid developed by Dr. L. C. Yang and discussed in Reference 15, a JPL report. During the initial three minute burn, the grid detected a few fibers, but following impact the grid was unable to count quickly enough and was soon shorted by fibers as the vacuum drew the air through the grid. Attempts to eliminate the shorting problem by increasing the grid voltage and by placing netting in front of the grid failed. As a result of the experience with the Ames Box, a new test fixture and procedure was developed which is discussed in the following section.

Open Air Burn Test

The purpose of the burn test of the carbon fiber composites was to determine the effects of each treatment on the number of

fibers released. The test results were evaluated in comparison to the number of fibers released by a state-of-the-art sample. (See Table VII.)

The number of fiber fragments released were counted by means of a detector, developed by Dr. L. C. Yang (Reference 15) for NASA LaRC, which is in turn connected to an integrator. This voltage was then sent to a recorder where a graph of counts versus time was generated.

The Y-axis scale on these graphs is as follows: zero is at the upper left hand corner and the count increases down. The maximum number on the Y-axis is limited by the size of the recorder. During many tests the recorder was re-set to zero in order to continue the counting. In these cases the maximum number of fiber fragments counted was the sum of fragments with respect to time. The graphs were calibrated to record twenty-four counts per inch on the Y-axis. The X-axis shows time increasing from left to right and depends on the sweep time of the recorder. The sweep time was generally set at fifty seconds per inch. Examples of these graphs are shown in Figures 9 and 10.

The results were fairly consistent even though many changes were made during the testing. The flame length was set at 2cm for the early tests (1-13), but once the propane cylinder was replaced, the longest length possible was 1.5cm. The rest of the tests were performed by another operator with a flame length of 1.5cm. The flame probably was positioned differently by the two people, which would cause the samples to burn at different rates.

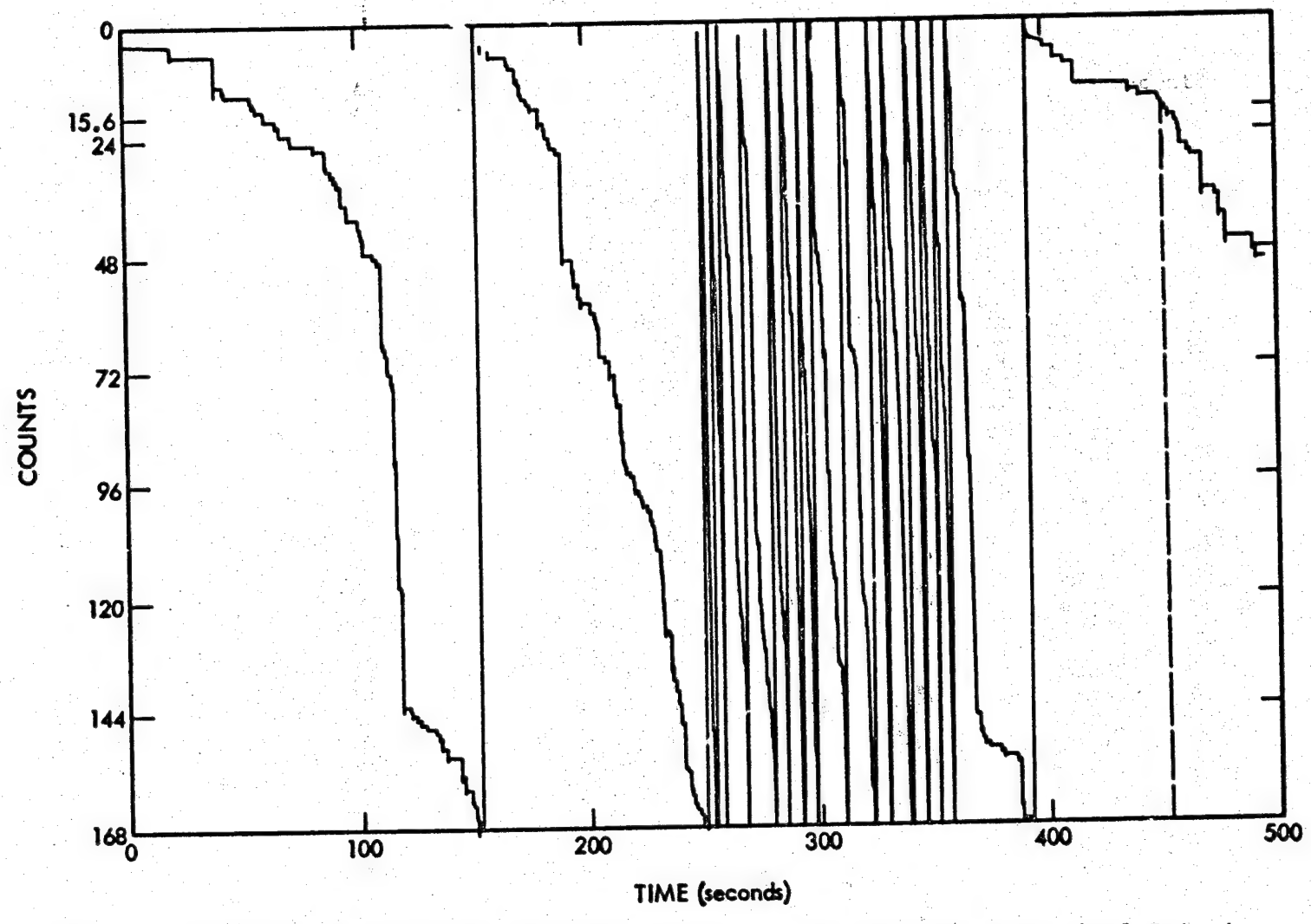

Fig. 9a. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #2; Sample 40; Treatment: None; Matrix: Fiberite 934

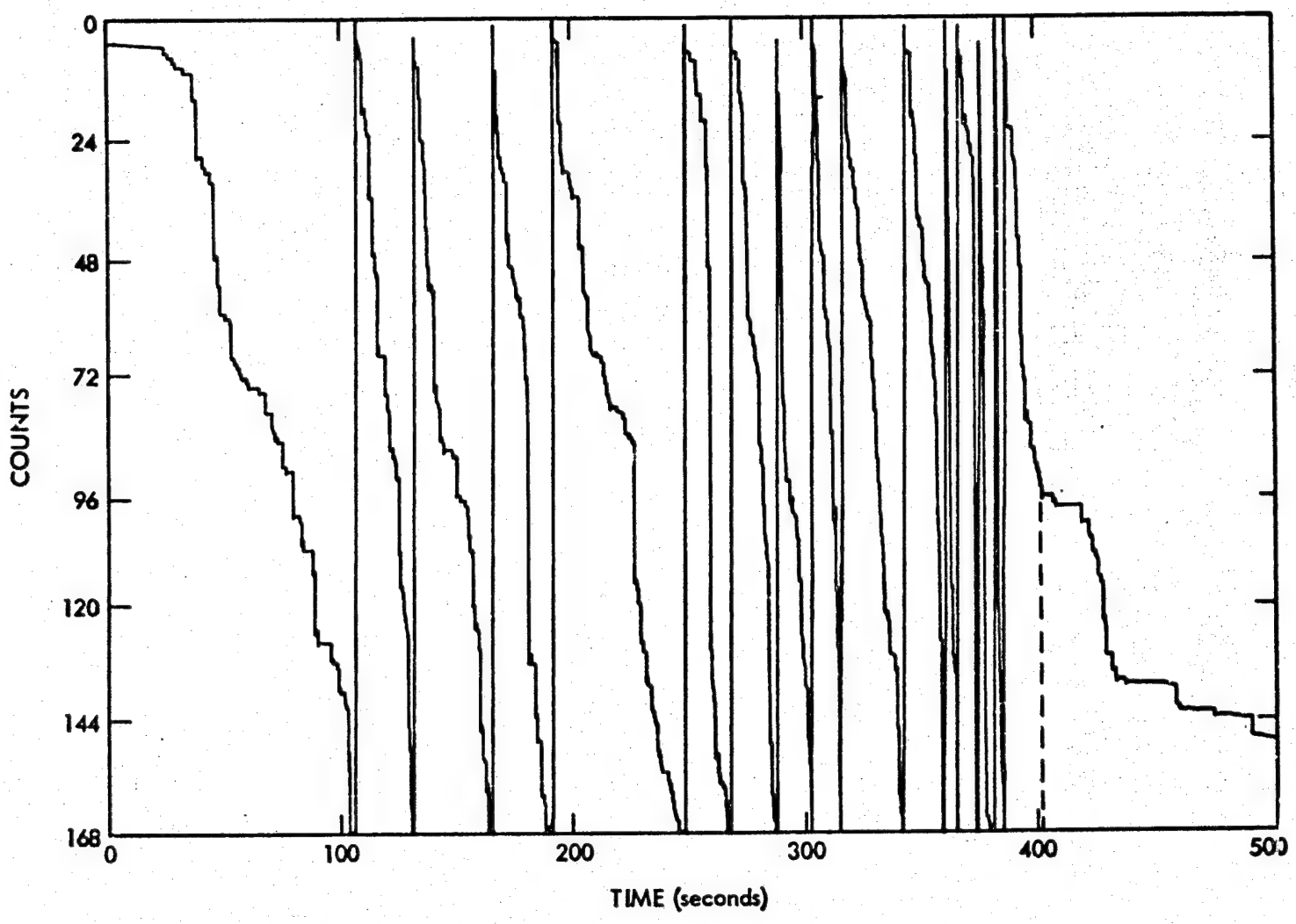

Fig. 9b. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #3; Sample 40; Treatment: None; Matrix: Fiberite 934

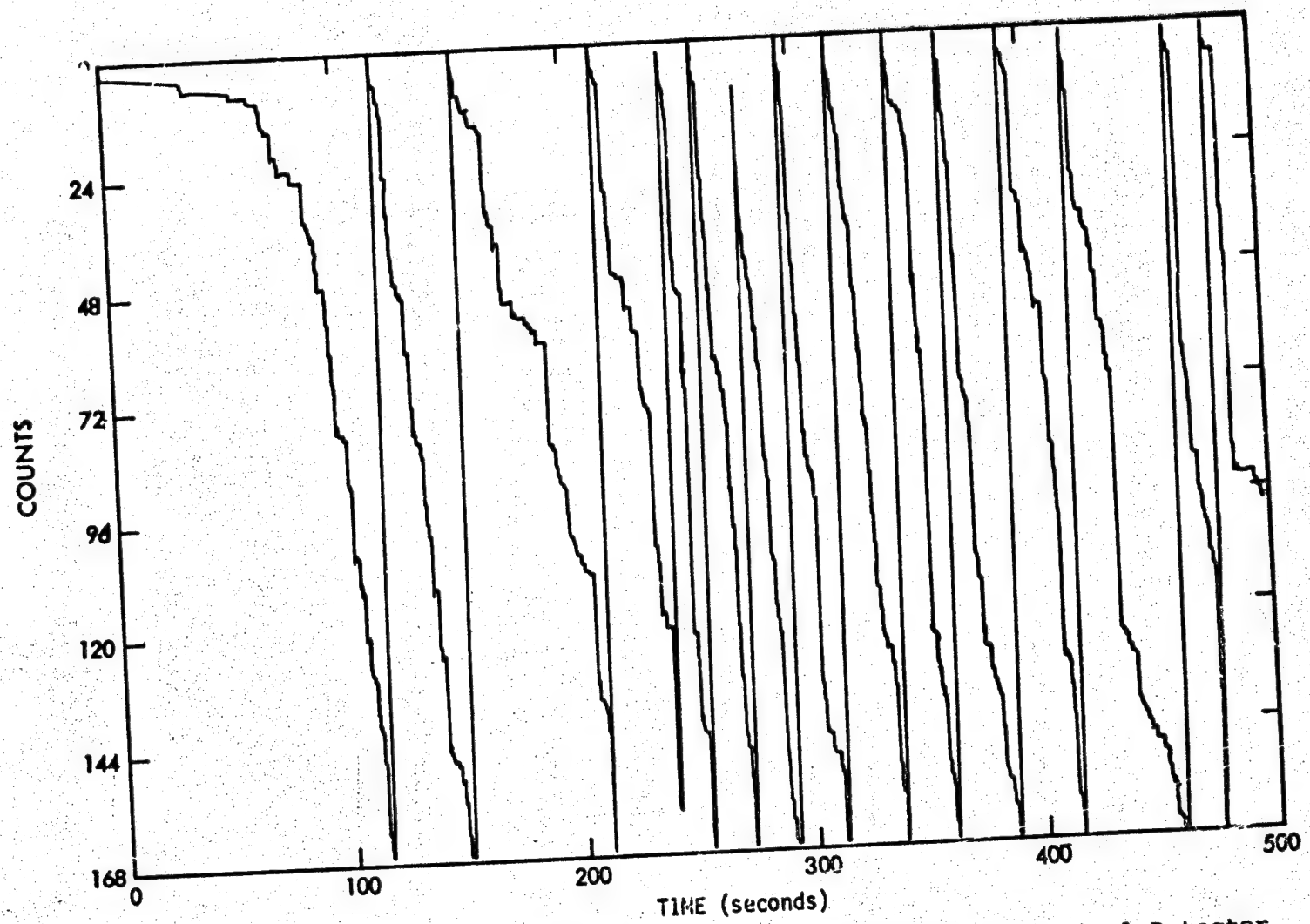

Fig. 9c. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #5; Sample 40; Treatment: None; Matrix: Fiberite 934

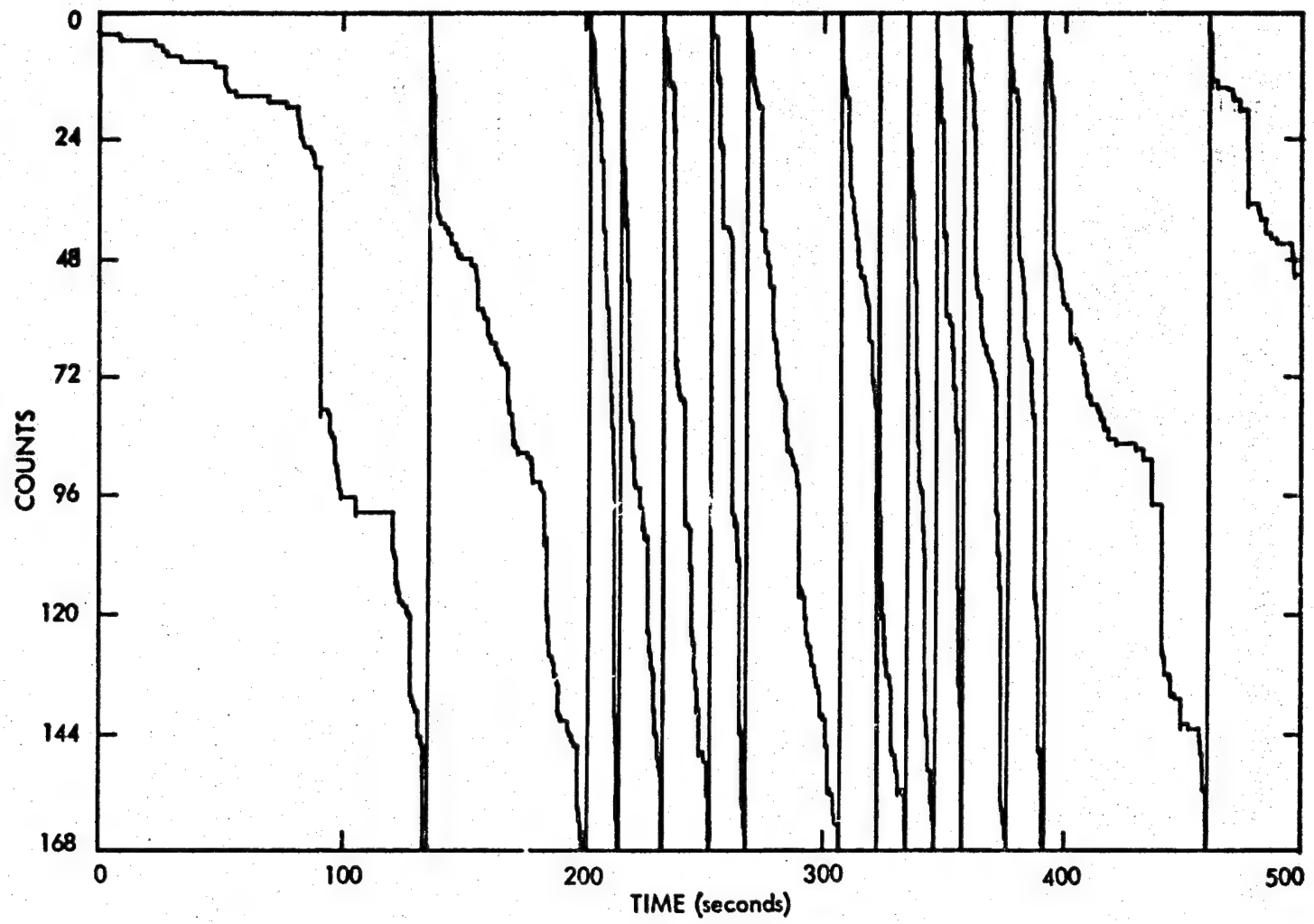

Fig. 9d. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #9; Sample 40; Treatment: None; Matrix: Fiberite 934

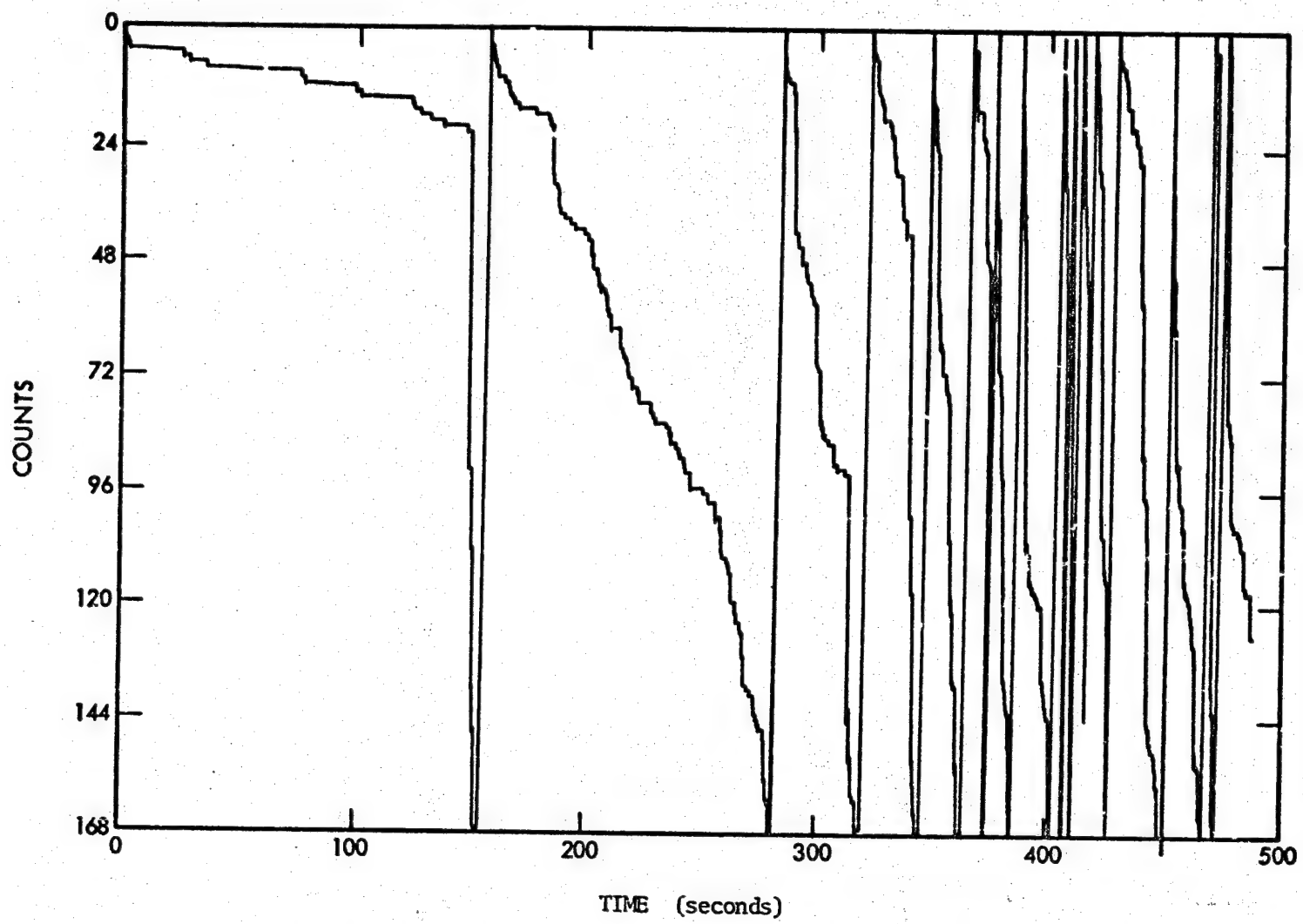

Fig. 9e. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #14; Sample: 40; Treatment: None; Matrix: Fiberite 934

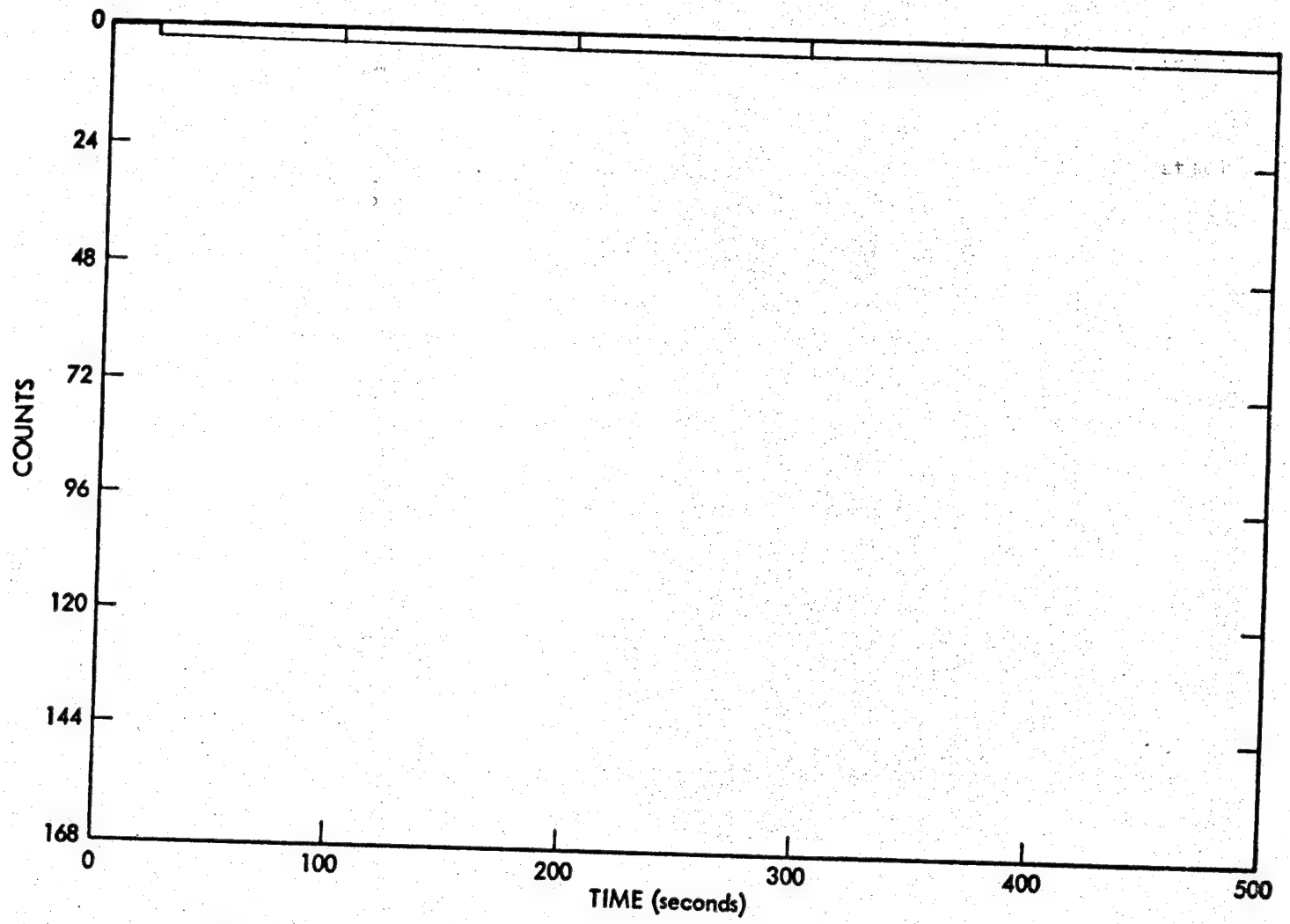

Fig. 10a. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #12; Sample 31; Treatment: CaAc; Matrix: Fiberite 934

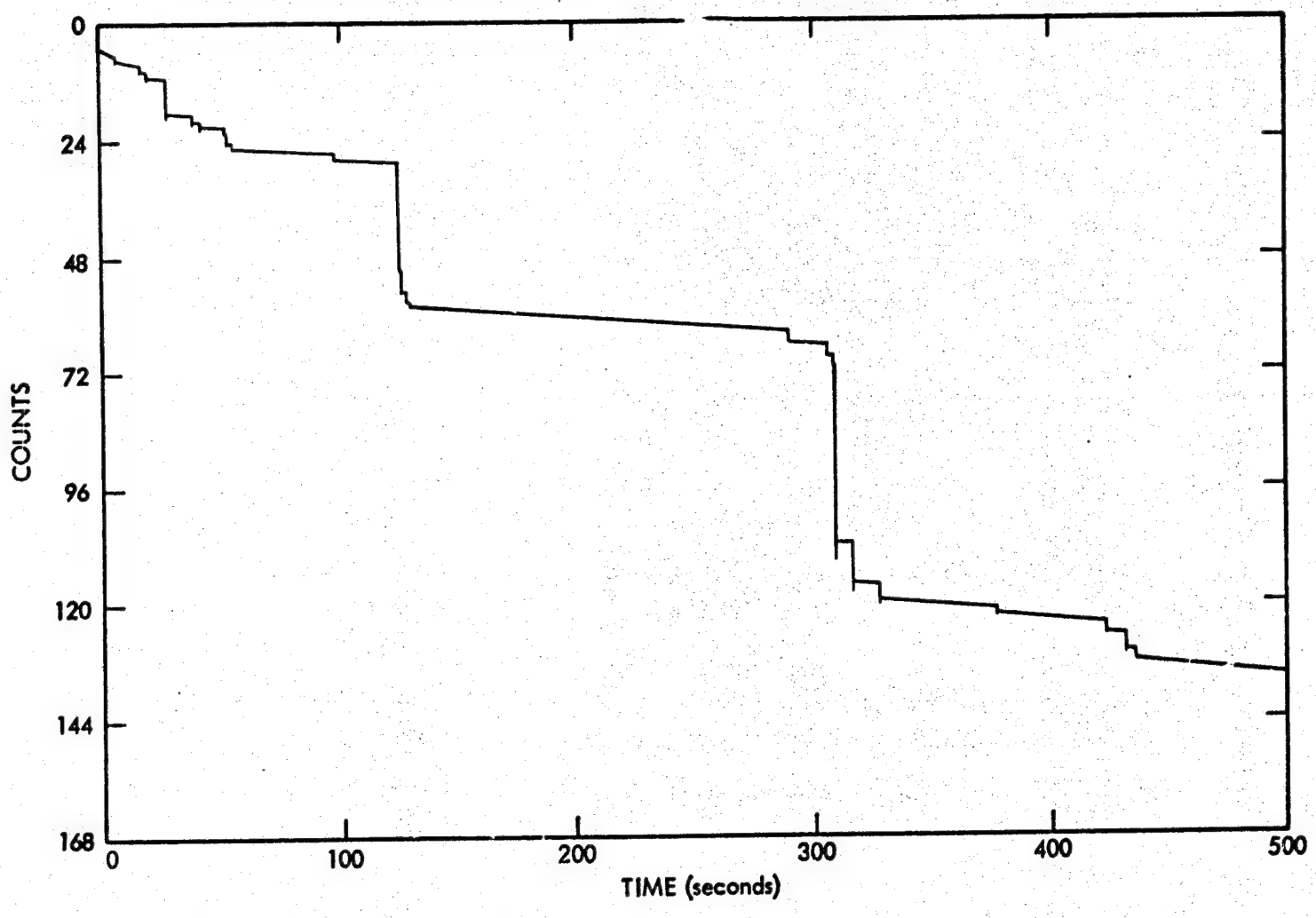

Fig. 10b. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #23; Sample 32; Treatment: CaAc; Matrix: Fiberite 934

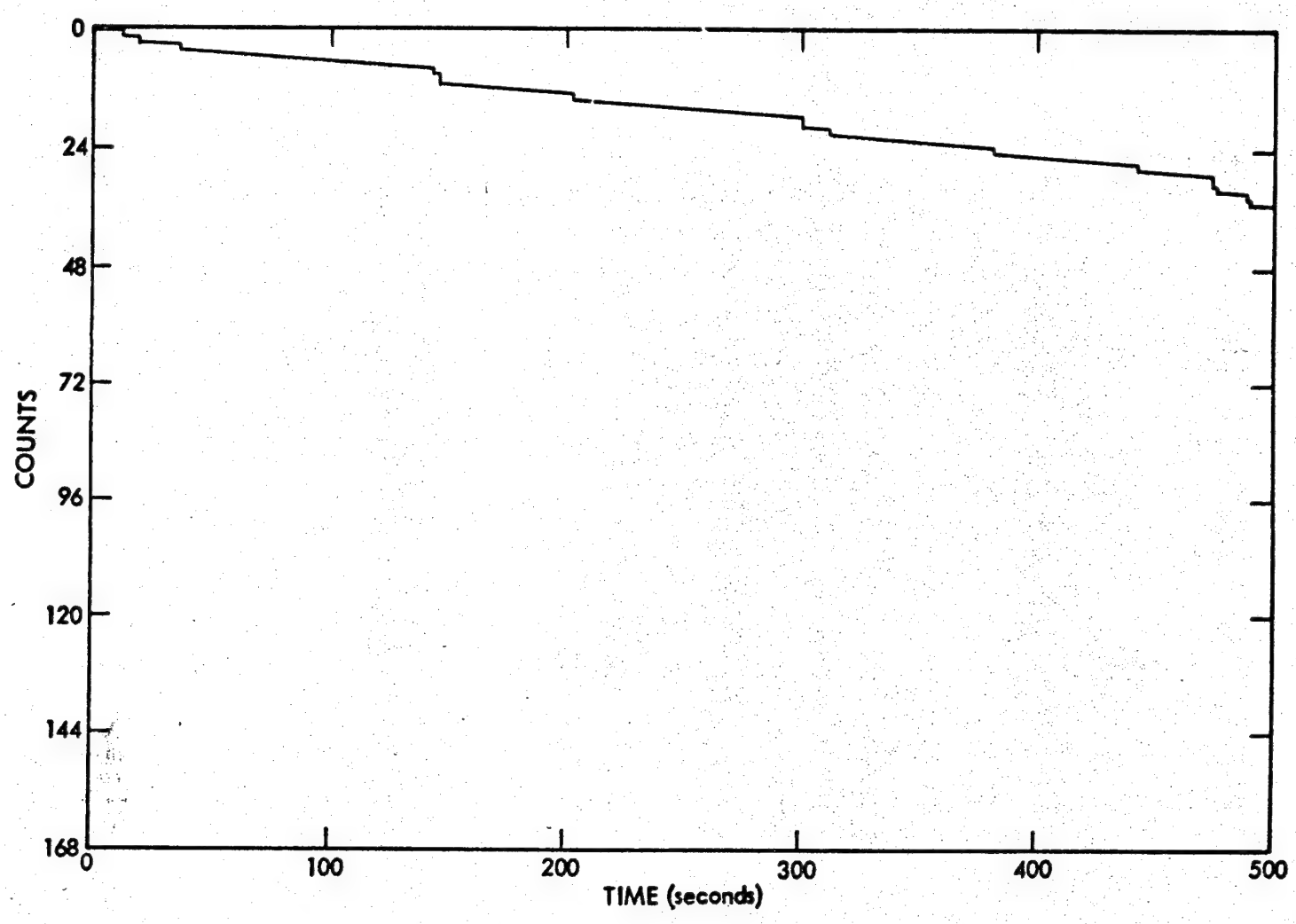

Fig. 10c. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #16; Sample 35; Treatment: CaAc+LiAc in Acrylic Acid; Matrix: Fiberite 934

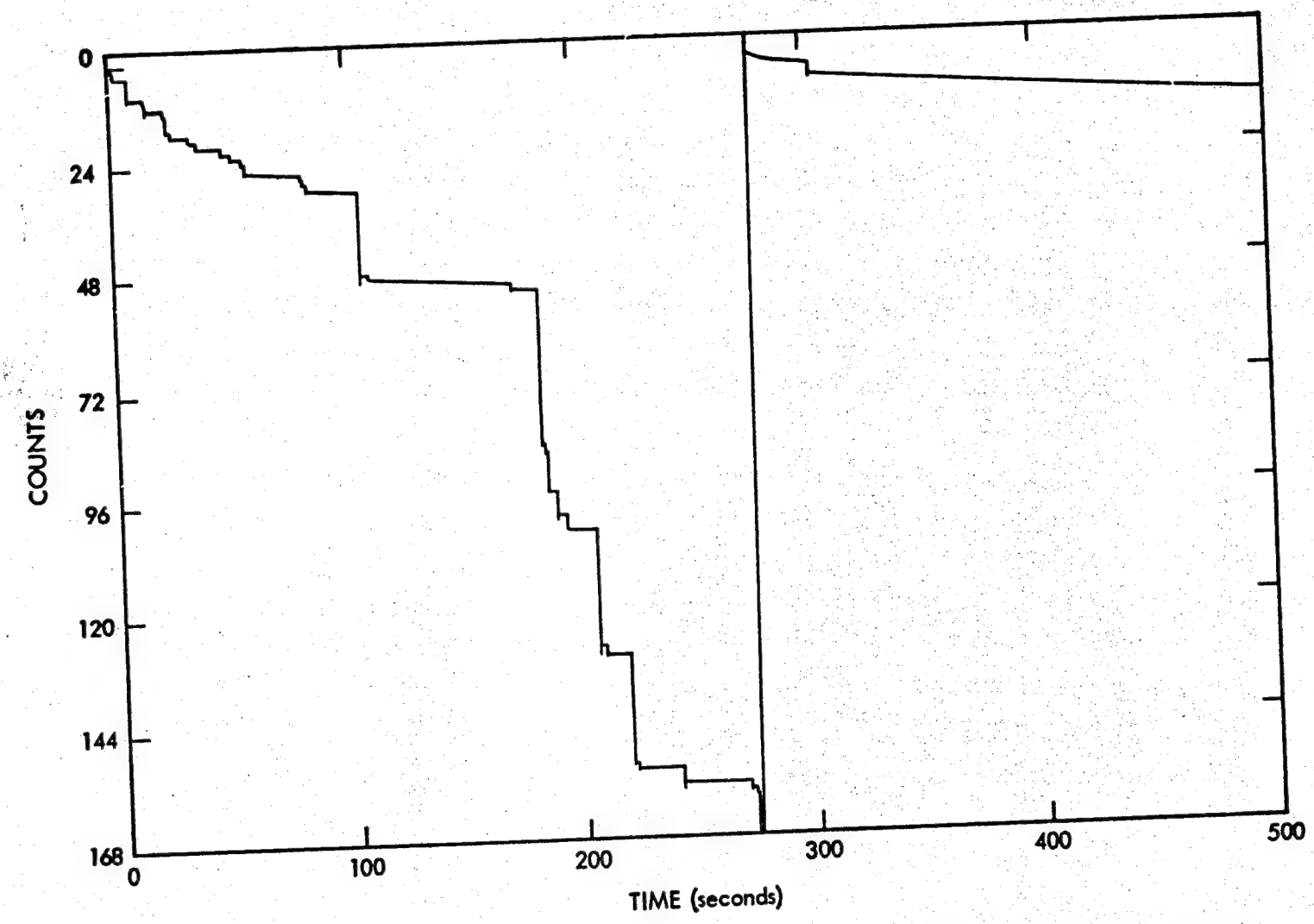

Fig. 10d. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #4; Sample 38; Treatment: 25% CaAc+75% LiAc; Matrix: Fiberite 934

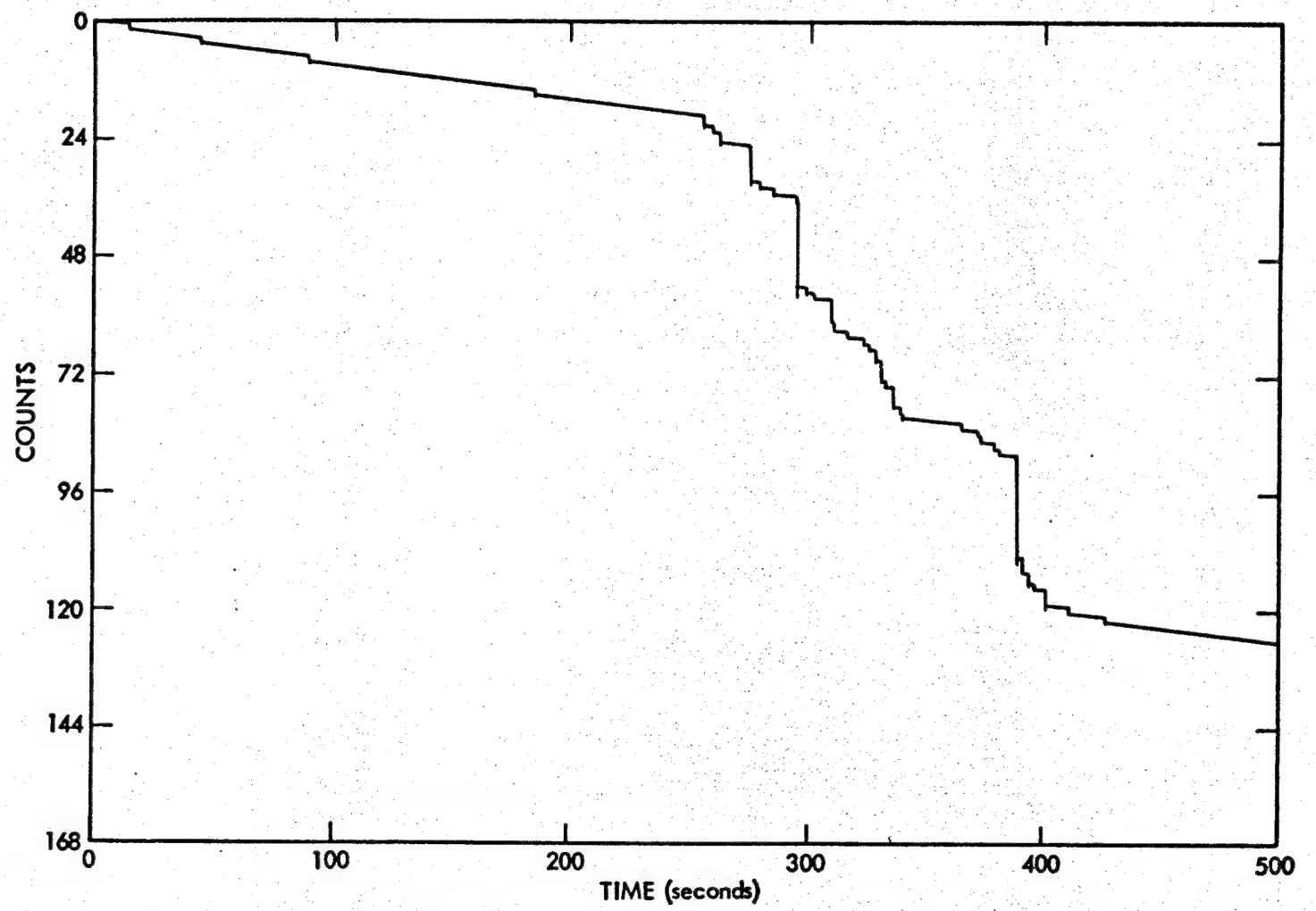

Fig. 10e. Example of the Fiber Fragment Counts in the JPL/LaRC Electrical Detector. Run #21; Sample 38; Treatment: 25% CaAc+75% LiAc; Matrix: Fiberite 934

The shaker table used initially was rated for approximately one pound of force with a maximum deflection of 3mm, unloaded. The original accelerometer and housing had a mass of 0.12 kg; this mass leads to a maximum acceleration of about 4g and a maximum deflection of 0.1 mm. It was desired to run the test at 10g with a deflection of 0.25 mm. Another shaker table was acquired which was rated for 127 newtons of force, and another accelerometer was necessary for measuring higher g forces. The new accelerometer and its housing had a mass of 0.12 kg. With the new shaker table and accelerometer, the maximum acceleration possible became 95g. The new accelerometer was calibrated by measuring the output voltage of a known calibrated accelerometer and of the new accelerometer. The output voltage of the known accelerometer corresponded to an acceleration; therefore, the output of the unknown accelerometer at the same input corresponded to that same acceleration. The tests were performed so that the acceleration on the sample was 10g (0.5V RMS output from accelerometer).

In order to make a quantitative comparison, the percentage of fragments released less than that for the untreated samples is shown in Table VI. (These values are based on the average values in Table VII.)

These values would imply that Sample 31 (25% CaAC solution) would be the best of those treated.

Table VI: Comparison of Burn Data Showing Improvement in Fiber Release With Treatment

Sample No.	Treatment	% Less Than Sample 40's
30	10% CaAc solution	99.2
31	25% CaAc solution	99.5
32	25% CaAc solution	93.7
35	20% Polyacrylic acid solution, then a 10% solution of:	98.9
	75% LiAc	
	25% CaAc	
38	Li/Ca Acetate	95.1

Table VII: Fiber Release Upon Burning for State-of-the-Art and Treated Composites

Sample No.	Test No.	No. of Counts in 450 Seconds
40	1	1815
(Untreated)	2	2830
	3	2546
Average Counts = 2040	5	2123
	7	666
	8	1250
	9	2307
	14	1980
	15	1676
	18	1532
	22	1498
	25	4252
38	4	176
(Li/Ca Acetate)	6	84
	21	120
Average Counts = 100	26	22
35	16	20
(20% Polyacrylic Acid Solution	24	26
10% soluton of: 75% LiAc		
25% CaAc)		
Average Counts = 23		
32	23	128
(25% CaAc Solution)		
31	12	2.4
(25% CaAc Solution)	13	3.6
	19	26
Average Counts = 11		
30	9A	15
(10% CaAc Solution)	10	33
	11	10
Average Counts = 16	17	8
	20	15

A comparison was attempted between these results and those of the Naval Research Laboratory (Reference 13). Although NRL also found calcium acetate to be a catalyst, no meaningful comparisons can be made due to the differing methodologies used in the preparation and testing of the samples.

IV. MECHANICAL AND AGING TESTS

The purpose of the mechanical properties tests was to determine whether the addition of catalysts to the surface of the carbon fibers was detrimental to the physical properties of the composite. Early in the search for proper test procedures, it was determined that a complete battery of tests, (tensile, compression, flexure, etc.) would be too time-consuming for the number of samples anticipated. Thus, a single test which would indicate whether the catalyst inclusion was harmful to the composite was sought. A telephone conversation with Dr. George Husman of the Air Force Materials Laboratory (Wright-Patterson AFB) resulted in the selection of the short beam shear strength test, ASTM D2344-76. The test measures the interply strength of composites which is the area most likely to be affected by changes in the fiber surface. It is a comparative test, not to be used for design criteria.

An Instron machine (Figure 11a) with 4,448 N tension load cell and a cage to change the direction of the force was used for the tests. A test jig was constructed according to specifications in the ASTM standards. The recommended span to thickness ratio for carbon yarn of four to one was used throughout the tests but the length to thickness ratio was increased to facilitate handling. Typical sample size was 2.5cm x 6mm x thickness, with the thickness generally measuring either 3mm or 1.5mm. Temperature and humidity were controlled by the building's air conditioning system (21°C, 25% RH) but was not recorded.

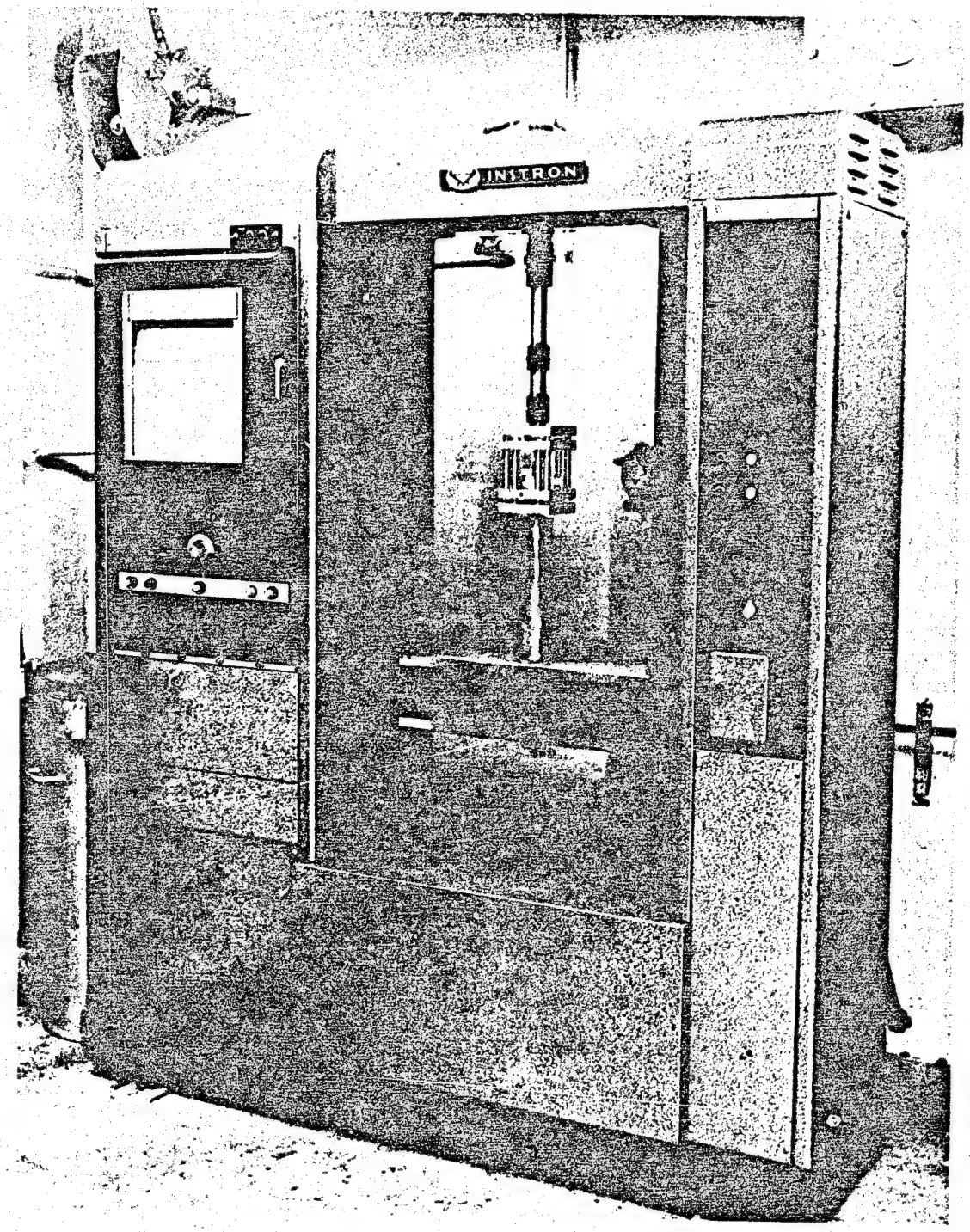

Fig. 11a. The Instron Testing Machine Used for the Determination of the Short Beam Shear Strengths

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The first tests conducted compared identically prepared ten-layer and five-layer woven samples. A sample Instron trace is shown in Figure 11b. The resin system was 80% RF-3000 and 20% RF-61 cured at 71°C. The results shown below indicate that five layers are sufficient for our purposes.

	SAMPLE NUMBER	NO. OF TESTS	SHEAR STRENGTH (10^6 N/m^2)	STANDARD DEVIATION (10^6)
10 LAYERS	1	3	44.38	1.27
5 LAYERS	6	3	42.67	2.39

After the test described above, a change was made in resin systems to Fiberite 934. Initial tests with the new system exhibited a large amount of data scatter. To eliminate the scatter a diamond-bladed bandsaw was purchased for cutting samples. It was thought that the superior cutting ability of the diamond blade would prevent splintering of the composite edges. No splintering was noticed with the new blade, but the data scatter persisted. A second approach was to determine whether the scatter was caused by the position of the sample in the panel; that is, were samples taken from the center of the panel stronger than those from edges? Figure 11c shows the cutting pattern for a panel made from Fiberite 934 prepregged woven cloth. The results indicated no effect of sample position on strength. The data scatter was accepted as random.

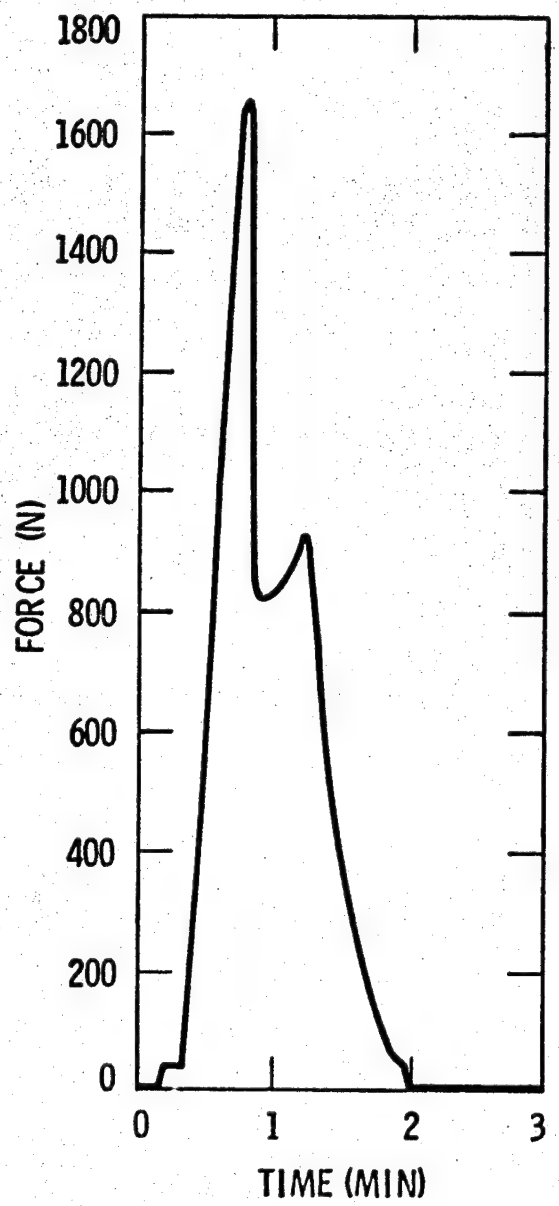
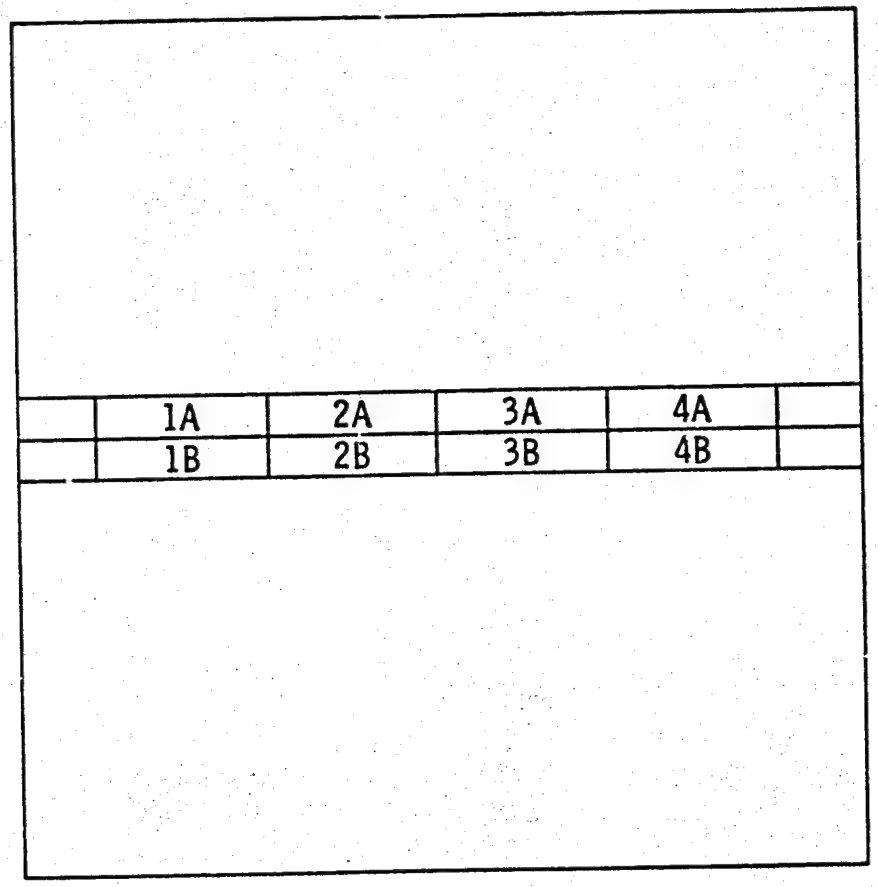


Fig. 11b. Sample Instron Trace for Short-Beam Shear Test
Crosshead speed was 1.27 mm/sec.

(T300 WOVEN PREPREGGED WITH FIBERITE 934 RESIN)



SHORT BEAM SHEAR STRENGTH (10^6 N/m^2)

1A - 47.58
1B - 61.39
2A - 54.17
2B - 51.90
3A - 52.52
3B - 59.32
4A - 68.53
4B - 53.66

Fig. 11c. Short Beam Shear Strength as Function of Sample Location

To confirm that the mode of failure in the short beam shear tests was inter-laminar shear, scanning electron micrographs of failed samples were examined. As can be seen in Figure 12, there is separation of the carbon fiber-matrix interface.

Although the majority of panels were prepared with Fiberite 934 resin, tests were performed with a number of different resin systems. As shown in Table VIII there are significant differences between resin systems with the Fiberite 934 exhibiting the highest value of inter-laminar shear. There are also differences caused by the form of reinforcement, whether unidirectional or woven carbon fiber is used.

The majority of the tests were concerned with the effects of catalysts on the inter-laminar shear strength. These tests can be divided into three areas: untreated panels, panels prepared by dipping fabric into solutions, and panels made with acrylic acid polymers. Table IX shows the results of the tests which indicate that the strength of the panels is decreased by the acrylate treatment and by dipping in calcium acetate solutions. However, the strength of panels prepared by dipping the fabric in combination of calcium acetate and lithium acetate was equal to the uncoated samples (compare results for samples 48 and 40 with samples 38 and 43).

In addition to the numerous short beam shear tests on all the candidate panels, four point bend tests (ASTM D790-71) were performed on a panel treated with 75% lithium acetate and 25%

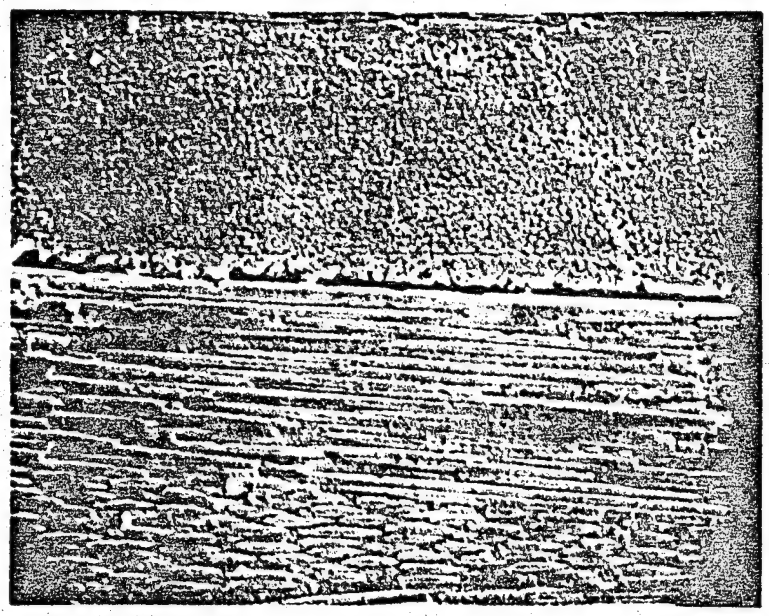


Fig. 12. SEM Photo of SBS Tested Composite Showing Separation of Fabric Layers

calcium acetate mixture on the woven fabric and on a state-of-the-art sample. The state-of-the-art had a strength of 8.28×10^8 N/m^2, while the treated sample achieved only 5.31×10^8 N/m^2.

A general view of the composite processing "Clean Room" is shown in Figure 13.

Aging Studies

Composite materials may have their physical and mechanical properties change during their service life. To a large extent, the changes will occur due to changes that the ingredient property values undergo and to changes in the quality of the interface between the matrix and the fibers. The matrix degrades in time

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due to thermal or chemical (frequently both) effects. Extensive investigations at the National Bureau of Standards by Madorsky have shown that the thermal degradation of most polymers can be characterized by Arrhenius-type equations. The thermal degradation is usually due to random scission of the bonds in the polymer. Among the chemical degradation mechanisms, oxidative degradation appears to be important.

Table VIII: Short Beam Shear Strength of Various Composite Samples

Sample Number	Number of Tests	Shear Strength (10^7 N/m^2)	Standard Deviation (10^6)	Comments
50	5	109.75	3.87	Fiberite 934 0° unidirectional prepreg
51	5	52.87 (Fiberite value is 67.60)	2.90	Fiberite 934 woven fabric
78-2	3	99.07 (Langley value is 119.30)	2.08	Hercules 3501 0° unidirectional prepreg, made by LaRC
--	3	24.11	1.68	Xylock-210 with woven fabric, made by ARC
--	3	27.94	0.69	90% RF-3000* 10% RF-61* woven fabric
--	3	38.96	0.41	80% RF-3000 20% RF-61 woven fabric

*These are the resin and curing agent respectively, supplied by E. V. Roberts Associates, Culver City, California.

TABLE IX: Short Beam Shear Strength of State-of-the-Art and Treated Composites

	Sample Number	Number of Tests	Shear Strength (10^6 N/m^2)	Standard Deviation (10^6)	Comments
Untreated	48	5	50.67	9.04	
	40	6	59.10	4.82	
Solution Dip	30	3	41.34	6.11	10% CaAc Sol Dip
	31	3	39.76	1.99	25% CaAc Sol Dip
	33	2	37.38	0.65	10% Sol of 50/50 Mix of CaAc and LiAc
	34	3	38.35	0.79	
	38	6	61.46	4.05	10% Sol of 25:75 Mix of CaAc and LiAc *
	43	8	50.95	2.99	
Acrylic Acid Treatment	42	5	47.56	3.00	Acrylic acid coated followed by dropping in 10% Sol. of 25:75 mix of CaAc LiAc
	44	3	25.55	1.67	
	45	3	20.86	1.18	

*Based on the retention of good mechanical properties (in contrast to the other treatments shown in this table) and the good electrical hazards alleviation, this 25:75 Ca:Li Ac treatment appears to be the best of those explored.

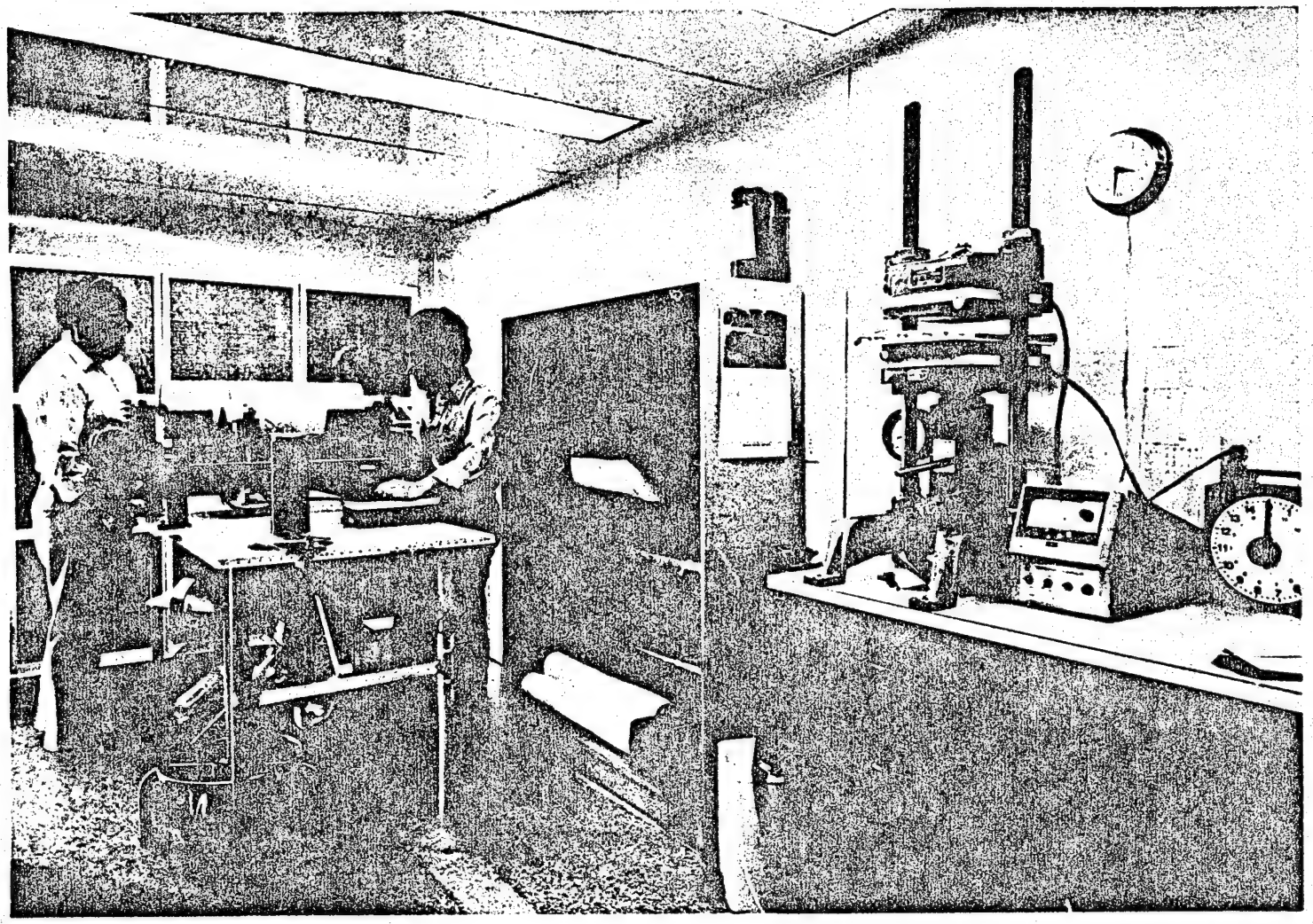

Fig. 13. The "Clean Room" Composites Processing Laboratory Showing the Drum Winder for Treatment Application, a Supply of the Fiber Cloth and the High Temperature Press (right foreground).

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It is of interest in these studies to determine the service life of the composites and more especially to determine how the catalytic treatment (for the electrical hazards alleviation) interferes with the useful service life. It is natural to suppose the inclusion of the catalyst in the composite would increase the basic degradation rate even at (normal use) standard temperatures. If this is indeed an important factor, the useful service life of the modified composites could be significantly shorter than the state-of-the-art composites. Thus the need is felt for some technique of determining the service life before the materials are put to use. The problem is essentially one of predicting the change in the fundamental properties with time.

Under the basic assumption of a first order Arrhenius degradation mechanism for the matrix, the normalized bond density is written

$$-\frac{dN}{dt} = N\,B\,\exp\,(-E/RT).$$

The limitations of using such a global equation for describing the complex heterogeneous reactions are clearly recognized. Its use is thought to be consistent with the general level of sophistication in conducting these experiments which are also global.

The above equation considers only the random thermal degradation and does not have information on the other possible effects due to chemical degradation or effects due to strain of the material (mechanical degradation). In the absence of thorough data, the basic aging equation may be written,

$$\frac{dN}{dt} = -\,N\,\phi\,(g,\,\varepsilon)B\,\exp\,(-E/RT)$$

where $\phi(g, \varepsilon)$ is some function of the geometry and strain in the material. One fact that emerges from considerations of molecular structures, the long chain entanglement, creep and related matters, is that there is no *a priori* justification for assuming that the results from aging studies at zero stress (strain) are indeed applicable for structures that are normally stressed in service life. Considerations of molecular structures and their relation to the ultimate material properties indicate that the ultimate stress of composites is related to the ingredient property values and the nature of the interface between the matrix and the fibers. If these effects are adequately handled by a function $fn(g, \varepsilon)$, the basic aging equation may now be written,

$$\boxed{\frac{1}{\sigma}\frac{d\sigma}{dt} = -\ fn(g, \varepsilon)\ B\ \exp(-E/RT)}$$

Here σ is the ultimate strength in any mode. Let us, for the moment, concern ourselves with the extensively used ASTM short beam shear tests. Thus σ is the short beam shear strength for the composite material. Given the nature of the function fn and the constants B and E, the service life can be predicted as the time needed for the degradation of the ultimate short beam shear strength by a predetermined amount (1%-5%).

It is obvious that under normal conditions the tests will have to last years, for any good composite would certainly have several years of useful life. In order to expedite laboratory

tests and to obtain a large bank of data within reasonable time, accelerated aging studies have been in use. The basic aging equation indicates that *temperature* can have a strong effect on the degradation and aging. Tests conducted at elevated temperatures can yield results that may be translated to service life under normal temperatures in a straightforward manner. Despite extensive work in the general area of service life prediction, a universally acceptable methodology does not appear to be available. The best available method appears to be the one given by Lewis et al. (Reference 14) on adhesive polymers. However, this method needs, as input values, the property values as a function of temperature.

The procedure followed in this investigation is to store the composites under zero and 50% ultimate strain at different temperatures, and to extract the samples after different durations of time to test their short beam shear strengths. The changes in the short beam shear strength as a function of temperature and as a function of time would enable a determination of the constants B, E and also the nature of the function fn in the basic aging equation. Either through calculations, or through direct extrapolation to normal service temperature of the high temperature data, the useful service life could thus be predicted.

Aging Tests

The short beam shear and open air burn tests showed that sample No. 38 had the greatest combined strength and fiber

release reduction. Therefore, this sample was selected along with sample No. 40 for accelerated aging tests. As in the mechanical properties tests, the aging study was to be a comparison of state-of-the-art and catalyst treated composites. The size sample used was the same as for the short beam shear test.

The aging tests were conducted using several variables: temperature, stress and moisture. Samples were examined at various intervals: 1 week, 4 weeks, 12 weeks and 16 weeks. Two temperatures were used, 26°C and 71°C. Testing for moisture was achieved by submerging the sample in a vial of water. The extensive R&D work sponsored by the Air Force in this critical area of water soak and sensitivity is acknowledged.

Stress was applied to simulate the conditions present in the short beam shear test. Stress was applied by a specially selected metal jig with a screw loader. Fifty percent of the initial breaking stress ($\approx 28 \times 10^6$ N/m^2) was desired. This was achieved by causing the same amount of deflection in the beam as in the short beam shear test.

The results of the temperature and stress tests are given in Table X. The data, from which there were no observable differences detected over the period of the aging tests, are graphed in Figure 14.

The treated samples used in the moisture study showed a sharp decrease in their short beam shear strength as shown in Table XI.

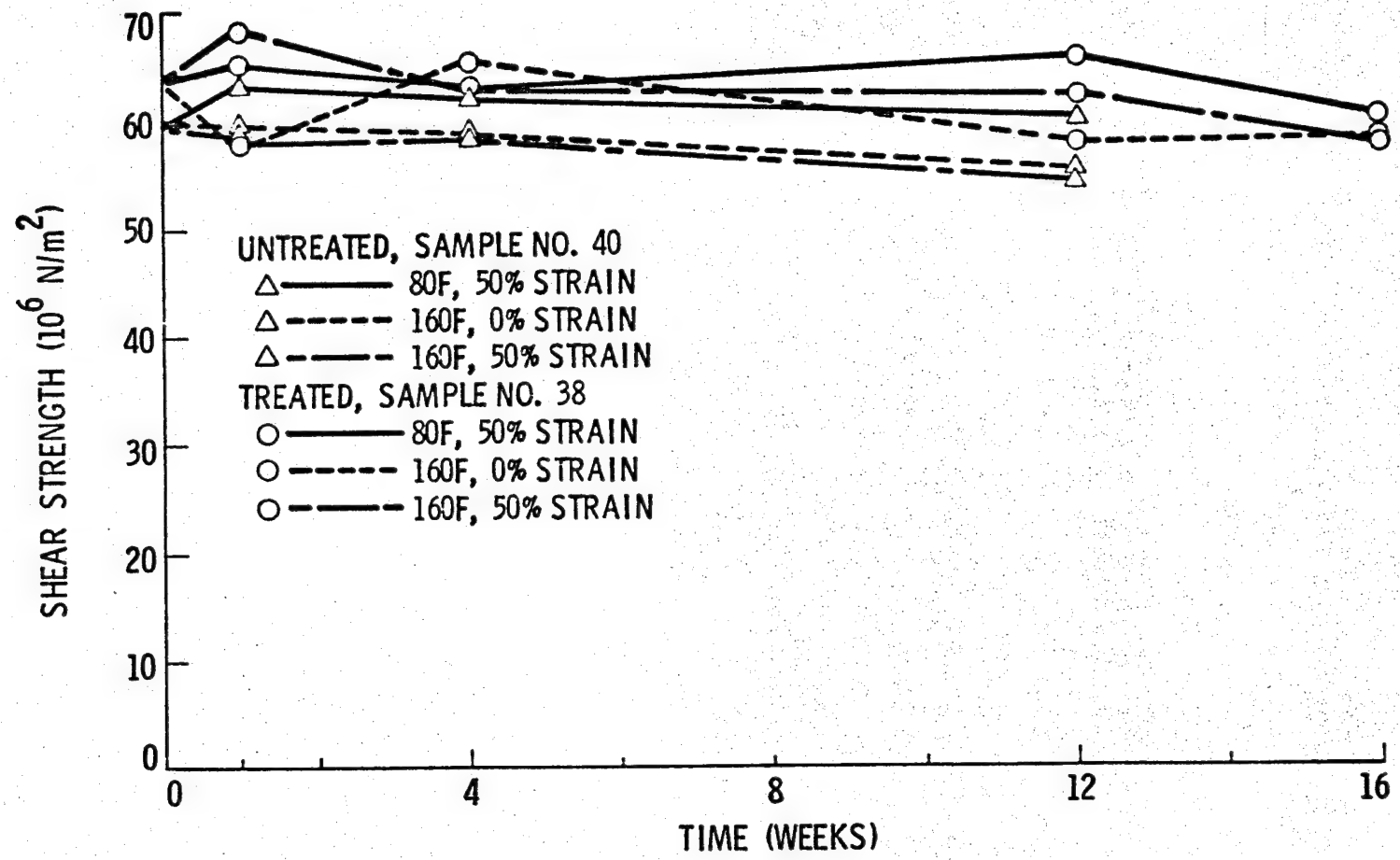


Fig. 14. Short Beam Shear Strengths of Composites as a Function of Time

Table X: Short Beam Shear Strengths (10^6 N/m^2) of Aged Composites (Standard deviation of tests is shown in parentheses.)

Time	Sample No. 40 Untreated			Sample No. 38 Lithium/Calcium Treated		
	26°C	71°C		26°C	71°C	
	50% Strain	0% Strain	50% Strain	50% Strain	0% Strain	50% Strain
Initial	59.10 (4.82)	--	--	61.46 (4.06)	--	--
1 Week	62.08 (7.79)	58.50 (8.30)	57.30 (8.26)	63.97 (4.16)	56.91 (8.95)	67.57 (3.92)
4 Week	60.86 (5.63)	57.91 (7.46)	57.84 (4.75)	61.79 (6.99)	64.58 (1.71)	61.37 (4.14)
12 Week	59.90 (5.81)	54.48 (7.48)	54.13 (8.85)	65.24 (3.64)	57.16 (5.98)	63.59 (12.1)
16 Week	--	--	--	59.59 (1.30)	57.87 (2.22)	57.22 (3.00)

The untreated samples, however, showed no significant change. The most probable cause of this effect is the solubility of the calcium and lithium salts used as the combustion catalyst. (The results are given in Table XI.) It is apparent that the formulation with the catalyst must be modified so that water-soaking does not affect the properties.

Discussion

Within the temperature range and stress levels, no discernible change is apparent either in the state-of-the-art or in the catalytically treated samples. The statistical spread (Table X) is in favor of this conclusion. Of particular importance is the relative change in the service life between the two families. None is apparent. Hence, based on this program of accelerated aging, the conclusion appears to be that the catalyst inclusion does not adversely affect the service life at normal temperatures and up to 71°C. In the tests that went up to sixteen weeks only the treated (three of the six) sets could be retained. Of these three, based on the averages of values till the 12 week period: the 50% strained sample shows 11% reduction in strength, the 0% strained sample at 71°C shows 3% reduction and the 50% strained sample at 26°C shows 6% reduction. More tests are needed before this 16 week data can be statistically interpreted. The effect of water-soaking has to be explored further. Also more detailed tests are desirable to augment the short beam shear strength tests in the general area of aging studies.

Table XI: Short Beam Shear Strengths (10^6 N/m^2) of Water-Soaked Composites.

(Standard deviation of tests is shown in parentheses.)

	Sample #48 Untreated	Sample #38 Lithium/Calcium Treated
Initial	50.67 (9.04)	61.46 (4.06)
1 Week	61.58 (4.90)	43.53 (0.80)
4 Week	58.01 (4.48)	41.49 (2.43)
12 Week	58.74 (4.87)	40.38 (1.69)

V. SURFACE-WETTABILITY AND THE ACRYLIC ACID POLYMER DEVELOPMENT

Application of Catalyst via Acrylates

Once calcium had been identified as one of the most effective catalysts, an effective method of application had to be developed. The original method of application used was to dip the woven fiber cloth into a solution of calcium acetate and let it dry. This method had a serious drawback, in that it was not possible to get a thin even coating of the catalyst on the fibers. The calcium acetate tended to clump together in some spots, leaving areas of the fiber that were uncoated. This caused uneven gasification of the fibers, resulting in large chunks of fiber flying off before they were completely gasified.

A solution to the coating problem was found by pre-treating the sample with a solution of polyacrylic acid. The acrylates are excellent film-forming compounds that are commonly used in floor waxes. The chain polymers of the acrylates can be cross-linked by any divalent metallic ion, in this case calcium (see Figure 15). This cross-linking resulted in an insoluble coating of the catalyst on the fibers.

The acrylate coating was applied by soaking the woven fiber sample (10 cm x 10 cm) in polyacrylic acid (Goodrite K-702, 20% solution in water). The sample was then blotted and dried for

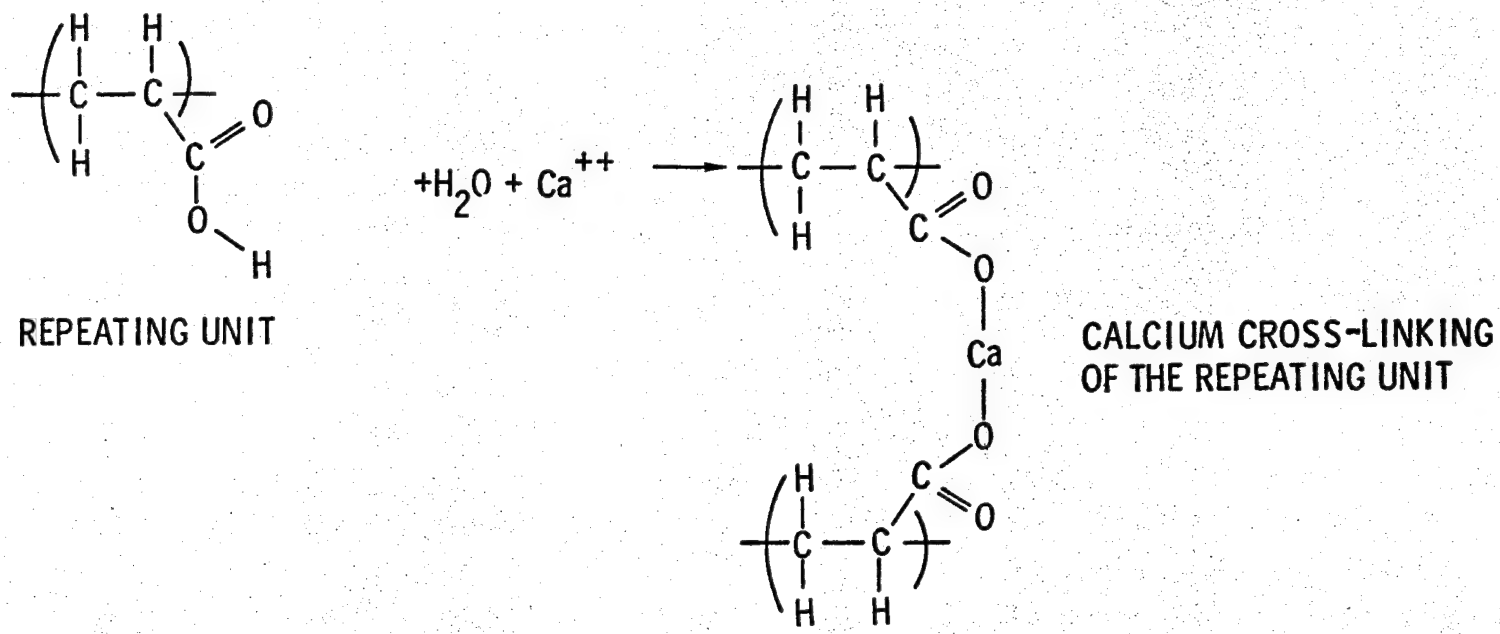


Fig. 15. Chemistry of the Polyacrylate Treatment

approximately two hours at about 120°C. After the acrylate coating had dried, the fiber was immersed in a boiling calcium acetate solution (10% by weight in water). The divalent calcium ion cross-linked the chains of the acrylate polymer, forming an insoluble coating. The fiber sample was then re-dried at 120°C. The sample was washed with distilled water to remove any calcium (in the form of calcium acetate) that had not reacted with the acrylate. Thus, the only addition to the original fiber sample is calcium acrylate. The averge weight gain due to the calcium acrylate was about five to six percent.

The even distribution of calcium throughout the sample was observed through the use of the Scanning Electron Microscope (SEM) as shown in Figure 16 where solution dip and acrylate treatment are compared.

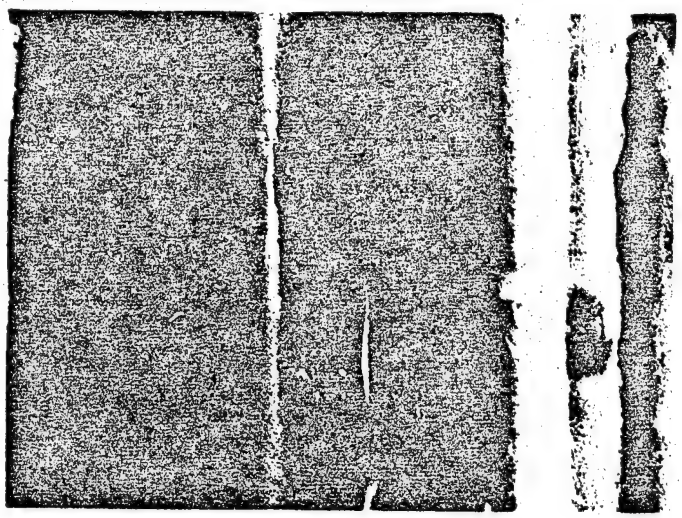
Improvement of Catalyst Through Use of Lithium

The addition of lithium to the calcium catalyst significantly improves the gasification of the treated carbon fibers. There is a definite improvement in both the solution-dipping method and the acrylate method.

When lithium is added (as lithium acetate) to the calcium acetate catalyst, the coating is improved in many ways. First, the resultant coating is a thin, even coating on the fibers, lessening the uneven gasification problem. Second, the

SAMPLE A 2KX

Calcium acetate catalyst treatment on
T-300 with simple solution dip.



SAMPLE 4A 2KX

Calcium acetate catalyst treatment
on T-300 with the acrylic acid vehicle

Fig. 16. SEM Photographs Showing the Vast Improvement in Catalyst Dispersion with the Acrylic Acid Vehicle.

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lithium forms a glassy substance when it is burned which tends to hold the fiber together until it is completely gasified. The third benefit due to the addition of lithium is the significantly lower weight gain due to the catalyst.

In the case of the acrylate treatment the main problem that arose was the excessive cross-linking of the polyacrylate chains by the calcium catalyst. When lithium is added to the solution, it uses some of the cross-link sites that had been used by calcium, resulting in a more flexible material. The advantage due to the lesser weight of the lithium/calcium catalyst are also present in this treatment.

The catalytic solution is made by mixing a 10% by weight aqueous solution of lithium acetate and a 10% by weight aqueous solution of calcium acetate. The ratio of lithium acetate to calcium acetate is 75 to 25. The catalyst may be applied to the carbon fibers either by solution-dipping or by the acrylate treatment. The solution-dipping process consists of dipping the fiber into the acetate solution and drying it for use in a composite. The acrylate treatment involves coating the fibers with a polyacrylic acid, drying the fibers and then reacting them with the boiling catalytic solution. The sample is then re-dried and ready for use in a composite.

The composites were tested for burning characteristics and physical properties. Gasification of the fibers was markedly improved by the use of lithium in the calcium catalyst.

VI. SUMMARY AND SPINOFFS

The basic objective of this work was to pursue tasks aimed at improving carbon fiber composites through process modifications; specifically it was the aim to alleviate the potential electrical hazards problem through *catalytic gasification* of the fibers in an aircraft crash-fire situation. The results reported here show that this basic objective was achieved.

In addition, it was necessary to pursue a series of tasks to show that the modified composites do meet the various requirements of structural composite materials. These included processing, mechanical and aging characteristics. The results obtained show that the processing of the composites at JPL is practically at a standard attained by the industry and other national laboratories. The modifications of the fiber and the composites to catalytically gasify the fibers have been effected in a manner that result in a small loss (10%) in the mechanical properties; the aging or the service life is not affected adversely. For even dispersion, the catalysts are included through a film-forming acrylic acid polymer over the fibers.

The catalyst selection itself was guided by a general theory of catalysis by Krylov. Elements in the periodic table were identified as possible catalysts. These include Group II metals. Based on a preliminary model of catalysis, the acetic acid salts

were tried. Calcium acetate was found to enhance the reaction rate of the fibers in air. Approximately 1.8% by weight of the calcium acetate (relative to the fiber weight) was found to be sufficient to completely gasify the fibers in air. The treated fibers, when ignited, glow and continue to do so, even upon removal of the heat source. The glowing reaction zone does not propagate to any area not originally exposed to the heat source. No gas phase flame is visible and only the mineral ash remains. These latter three characteristics are desirable from the point of view of not rendering the material less fire safe in attempting to solve the electrical hazards problem. By contrast, the state-of-the-art, "as received" fibers do not self-sustain combustion in air when the source of heat is removed.

Synergistic effects have been found among catalysts. The synergism has to do both with the enhancement of the reaction rate itself and with the behavior of the residue (mostly mineral matter). A mixture of calcium and potassium acetate tested in a Differential Scanning Calorimeter has been found to be far more effective in producing exothermic reactions in carbon particles compared to either salt alone. The other type of synergism has been identified between calcium and lithium salts. The addition of lithium has shown that the melting point of the complex residue is lowered sufficiently for a melt to form on the fibers. This melt layer holds together the fibers which otherwise have a tendency, sometimes, to break loose from the bundle and fly off. Here, the addition of lithium salts has proved invaluable. The

lithium acetate in combination with the calcium acetate forms a complex with the reaction products. This complex melts and flows around the fibers to hold them together. This type of synergism has proved very valuable in preventing fiber release in catalyzed carbon fiber composites.

The general problem of nonwettability of carbon/graphite surfaces has been overcome through the development of an acrylic acid polymer system with chemically bonded catalyst atoms in the polymer. This acrylic acid polymer system is seen to disperse the catalyst uniformly over the surface.

The mechanical property, as determined by the ASTM short beam shear test, shows compatible values to the state-of-the-art composites manufactured elsewhere. The catalytically treated composites show approximately ten percent deterioration in the mechanical property. Ways to regain this lost strength can be pursued.

In an attempt to determine the effect of the catalytic modification upon the service life of the composites, accelerated aging studies were conducted. The composite samples are stored for programmed lengths of time at elevated (71°C) and normal (26°C) temperatures under both zero and stressed (50% ultimate shear) conditions. The short beam shear strengths of the samples aged thus show no discernible change in the mechanical properties. Thus, it is concluded that the catalytic enhancement of fiber reactivity does not appear to adversely affect the service life of the composites.

The fiber fragments release characteristics of the composites wre determined (i) in the NASA ARC "Burn-Bang" box and (ii) in the JPL/LaRC high voltage grid destructor. The fiber fragments and the composite debris collected in the Ames box are available for analyses. The real time in situ count in the JPL/LaRC apparatus shows that hardly any conducting fibers were released in the treated composites while substantial quantities of fibers were released from the state-of-the-art composites. Based on the processing, mechanical properties and the electrical hazards alleviation taken together, a mixture of calcium and lithium acetates has been found to be a very effective treatment.

Fundamental studies pursued under Contract No. 955236 at Pennsylvania State University identified basic mechanisms in the reactivity of carbon fibers in air. Surface area measurements by gas adsorption techniques reveal that the pore structure of the fibers may have an important effect upon their reactivity. Treatment in nitric acid has shown a great improvement in subsequent susceptibility to catalytic enhancement of reactivity by Group II metal salts.

The following areas have been identified for further study. Some of these are in areas of general national concern.

(1) Composite Materials

The effect of compositional variations in the fibers has to be studied, particularly sodium, which has been reported to vary over a rather wide range as an "impurity" in the fibers. The reactivity of the fiber in air is dependent upon the sodium content. A systematic study is needed to answer questions with regard to the effect of sodium on the long term reactivity of fibers.

Chopped fiber composites have been suggested as possible for greatly reducing the processing time. Instead of random fiber orientations that would occur under ordinary conditions with composites, extrusion through a ribbon-former (much like in propellants) can be followed. The initial data shown in Table XII indicate that the short beam shear strength of the cast composites is close to that of the unidirectional fiber layup composites. More research is needed to optimize the ratio of useful fraction to the total material used in such cast composites.

Considering the prevailing thoughts that most of the strength and stiffness of the fibers come from the highly graphitic and oriented outer shell with a lesser contribution from the inner core, hollow fibers are suggested for vastly improved strength-to-weight and stiffness-to-weight ratios of structures. Processing of the fibers starting with available hollow precursors is suggested as a promising area for further research.

Table XII: Comparison of State-of-the-Art Unidirectional and Cast Composites.

SAMPLE NO.	MATRIX	SHORT BEAM SHEAR STRENGTH (10^6 N/m^2)	
50	Fiberite 934	109.75	State-of-the-art
78-2	Hercules 3501	99.075	State-of-the-art
CF-1	Fiberite 934	100.21	Cast Composite

For effective utilization of the matrix fiber system (where the matrix is obviously the weaker component), prestressing the composites during processing is suggested. Such prestressing can result in more effective utilization of the matrix-fiber combination up to the ultimate load. Larger deformations at failure (a highly desirable characteristic for commercial or non-military vehicles) have been seen in the preliminary work at JPL on prestressed composites on an equal weight basis.

(2) General Area of Carbon Reactivity

The particulates exhaust problem from the Diesel automobile has been identified as an issue of national concern. The powerful catalysts found in this study for carbon/graphite oxidation and combustion may hold promise for catalytic gasification of such carbon particulates from Diesels.

Coal combustion is another area of national concern. The catalysts found during the course of this study have shown applicability to coal catalytic combustion also. There are indications that catalytic enhancement of coal combustion could result in smaller furnaces for a given throughput rate and lower pollutants also.

In conclusion, the present work on the catalytic enhancement of carbon fiber reactivity through process modifications has indicated promising areas for further research besides alleviating the electrical hazards problem of carbon fiber composites.

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APPENDIX 1

STUDY AND MODIFICATION OF THE REACTIVITY OF CARBON FIBERS

Final Report No. 1

P. L. Walker, Jr.
I. M. Ismail
O. P. Mahajan
T. A. Eapen

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Contract No. 955236

The Pennsylvania State University
University Park, PA 16802

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ABSTRACT

Enhancement of the reactivity to air of polyacrylonitrile-based carbon fiber cloth has been achieved by the addition of metals to the cloth. Prior to metal addition, the cloth was oxidized in 54 wt% nitric acid in order, both, to increase the surface area of the cloth and to add carboxyl groups to the surface. Metal addition was then achieved by soaking the cloth in metal acetate solution to effect exchange between the metal cation and hydrogen on the carboxyl groups. The addition of potassium, sodium, calcium, and barium enhanced fiber cloth reactivity to air at 573 K. Extended studies using potassium addition showed that success in enhancing fiber cloth reactivity to air depends on: extent of cloth oxidation in nitric acid, time of exchange in potassium acetate solution, and the thoroughness of removing metal acetate from the fiber pore structure following exchange. With increased potassium loading on fiber cloth which has undergone a fixed extent of prior oxidation, cloth reactivity in air reaches a maximum and in some cases decreases. Optimum loading is associated with potassium added by exchange; additional loading is associated with potassium added by decomposition of acetate not removed from the fiber pore system by washing. Cloth reactivity increases essentially linearly with increase in potassium addition via exchange.

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SUMMARY

The purpose of this experimental study was to enhance the reactivity to air of carbon fiber cloth, supplied by Woven Structures using polyacrylonitrile-based T-300 carbon yarn produced by Union Carbide. The approach used to enhance reactivity was to add metal catalysts to the cloth by ion exchange. Prior to exchange by contacting the cloth with metal acetate solutions, the cloth was oxidized at 388 K in 54% nitric acid solution to increase the surface area of the cloth and to add carboxyl groups to the surface.* Metal addition was then effected by exchanging the metal cation with the hydrogen on the carboxyl groups at 343 K. Reactivity of the metal-loaded fiber cloth was studied in 0.1MPa of air at 573 K. Reactivity was enhanced by the addition of potassium, sodium, calcium, and barium. Extended studies using potassium showed that success in enhancing reactivity depends upon a number of variables. Variables investigated were: (i) extent of cloth oxidation in nitric acid, (ii) time of exchange in potassium acetate solution, and (iii) thoroughness of removing metal acetate from the fiber pore structure following exchange. It is shown that there is an optimum potassium loading at each oxidation level, associated with potassium added by exchange. Further loading by potassium originating from the acetate not removed from the pore system by washing can in some cases lead to a decrease in cloth reactivity in air. For the maximum reactivity achieved, carbon burn-off in 8 hr at 573 K was increased from <1% for the as-received fiber cloth to 75%. Potassium loading on the cloth was 0.79 wt%.

It is concluded that carbon fiber cloth reactivity to air can be sharply increased by cation exchange once the accessible surface area of the fiber has been increased and carboxyl groups added to its surface by oxidation in nitric acid. The limitation of the method is that fiber cloth oxidation will lead to reduced strength and modulus in the cloth. Therefore, it is expected that there will be an optimum degree of oxidation where both fiber cloth reactivity and mechanical properties of composites fabricated from the cloth are enhanced.

* Note: It is well known that treatments such as those with HNO_3 tend to increase the polar character of the fiber surface, which may decrease the environmental stability particularly with respect to moisture. This aspect needs to be studied further.

1. INTRODUCTION

Concern has arisen over the potential for accidental release of carbon fibers from resin matrix composites should the composite become involved in a fire (1). Thus for some applications there is interest in enhancing the reactivity of carbon fibers to air.

It is known that reactivity of carbon to oxidizing gases can be increased by increasing the active surface area (ASA) of the carbon and by adding inorganic catalysts to the carbon (2,3). There have been a number of studies on increasing the surface area of carbon fibers using oxidative etching in order to subsequently enhance their bonding to the resin matrix (4). Probably the use of nitric acid has been the most common (4-7). Until recently, inorganics have been added to carbon primarily by impregnation of the carbon with a salt solution, followed by drying, and decomposition of the salt (3). More recently, it has been shown that well dispersed inorganics (cations) can be effectively added to carbons using ion exchange with the hydrogen on carboxyl groups (8). This has been the approach used in this study in an attempt to enhance fiber reactivity to air.

2. EXPERIMENTAL STUDIES

2.1. Materials

Studies were made on carbon fiber cloth woven by Woven Structures, Inc. from T-300 carbon fiber yarn grade WYP 30 1/0 manufactured by Union Carbide (9). The polyacrylonitrile-based (PAN) yarn consisted of 3000 filaments (7μm in diameter) in a one-ply construction. The surface was treated with about 1.0-1.5 wt% proprietary sizing. Selected properties of the fibers in the cloth are given in Table 1. The small crystallite size (L_c) of the fiber cloth and its high nitrogen content (that is, 6.5 wt%) is consistent with its having been heated to less than 1800 K (10,11). Preferential basal plane alignment along the fiber axis results in a low surface area for the fibers, as measured from Kr adsorption at 77 K (using the BET equation), and a small amount of porosity accessible to helium at room temperature. In fact, the Kr surface area of 0.37 m^2/g agrees well with the geometric area of the filaments (0.33 m^2/g) based on a diameter of 7μm and density of 1.71 g/cm^3. It is significant that the fibers had a substantial total pore volume as calculated from x-ray and mercury densities, that is a total porosity of 20%, but that about 78% of the total pore volume was inaccessible to helium.

A semi-quantitative spectroscopic analysis of inorganic elements present in the fibers in the cloth is given in Table 2. Consistent with the findings of others (12), the concentration of sodium* is found to be considerably higher than that of any other metal in the treated PAN fibers.

*In discussions with JPL personnel, they report finding wide variations in sodium content in PAN fibers. It is to be emphasized that our analysis was on just one batch of T-300 fiber cloth. Variations in sodium content in PAN may be due to such variables as: type of initiator used in polymerization, whether a sodium compound was present during the PAN spinning operation, and cation content in the wash water.

2.2. Oxidative Etching

Different weights of cloth were refluxed in 54% HNO_3 solution (normality of 11.7) at about 388 K for 10 hr to: (i) increase the fiber accessible total surface area and ASA and (ii) add carboxyl groups to active carbon sites. Even for the highest cloth to solution ratio used (30 mg cloth/cm^3 solution), the acid concentration of the solution was still high following oxidation; that is, it had a normality of 10.2. Oxidized samples were washed with distilled water under refluxing conditions for 40 hr and then dried at 383 K.

2.3. Ion Exchange

Replacement of hydrogen on the carboxyl groups of the HNO_3-oxidized fibers by metal cations was accomplished by shaking about 0.25g of fiber cloth in a 50 cm^3 2.0 molar solution of metal acetate in a N_2 atmosphere at 343 K for various periods of time. The procedure is described in more detail elsewhere (13). Following exchange, the samples were washed either in flowing, cold distilled water or by refluxing in hot distilled water for varying periods of time.

2.4. Reactivity Measurements

Reactivity of fiber cloth samples to 0.1 MPa of dried air was measured using a Fisher Model 460 TGA unit. About 5 mg of sample were held in a platinum pan, suspended from a Cahn electrobalance. In all cases, samples were first heated to 383 K at a rate of 20 K/min in N_2 and held for 30 min to remove weakly adsorbed water. For reactivity runs at 573 K, heating was continued in N_2 at 20 K/min up to temperature and held for 30 min before switching to air. Rates of burn-off at 573 K were expressed on a dry-ash free basis, that is following removal of water at 383 K. Gas flow rate through the reactor and sample weight in the platinum pan were such that an external gas mass transport effect on reactivity was absent (2).

3. RESULTS AND DISCUSSION

3.1. Nitric Acid Oxidized Fiber Cloth

Oxidation of carbon fiber cloth in nitric acid decreased the level of inorganic impurities, increased surface area, reduced cloth reactivity to air, but produced a negligible change in L_c or interlayer spacing within the crystallite. For example, oxidation for 10 hr, using a cloth to HNO_3 ratio of 6.0 mg/cm^3, reduced the sodium concentration from 0.2 to 0.03 wt%, calcium below 0.03%, and barium below 0.003%.

As seen in Table 3, surface area development depends upon the ratio of weight of fiber cloth oxidized to volume of acid used for a 10 hr oxidation time. Surface areas were measured using Kr adsorption at 77 K and the BET equation with 30 min allowed for equilibration of each adsorption point. Outgassing temperatures between 383 and 573 K prior to adsorption had a

negligible effect on Kr adsorption. The particularly large increase in surface area in going from a cloth to acid ratio of 6.6 to 6.0 mg/cm^3 was accompanied by a significant change in the chemical analysis of the fiber cloth. That is, the original cloth and those oxidized using cloth to acid ratios of 6.6 and greater had carbon contents between 93.2 and 88.4%, nitrogen contents between 6.3 and 6.8%, negligible hydrogen and sulfur, and the remainder oxygen and water. The cloth oxidized using a cloth to acid ratio of 6.0 had the following analysis: C, 70.9%; N, 4.9%; H, 0.73%; and balance, 23.5%. Obviously there is a large increase in oxygen and water content in this sample; but oxidation added negligible additional nitrogen to the cloth, for example as nitro groups.* Heating the sample to 383 K in N_2 resulted in a weight loss of 11% which is attributed primarily to release of water which was hydrogen bonded to oxygen functional groups on the fiber cloth surface. Further heating of the sample to 573 K in N_2 resulted in an additional weight loss of 10% of the dried fiber cloth, which is attributed primarily to loss of CO_2 following decomposition of carboxyl groups from the fiber surface (15).

Assuming that 12.5% of the oxidized fiber cloth (Sample D) is oxygen in the form of carboxyl groups and that each carboxyl group occupies an area of 0.083 nm^2 (associated with an active site in the prismatic surface of a carbon crystallite), the area occupied by carboxyl groups is estimated to be 195 m^2/g. This area is considerably in excess of that measured by Kr adsorption at 77 K on this sample and suggests molecular sieving (16). That is, HNO_3 at 388 K was able to penetrate significant pore volume which was inaccessible to Kr at 77K. Or possibly HNO_3 gained access by swelling the fiber. That oxidized fiber cloth sample D was a molecular sieve was further confirmed by measuring CO_2 uptake at 298 K. From the Dubinin-Polanyi plot (17), a micropore surface area of 139 m^2/g is estimated, again a value considerably in excess of the area measured by Kr adsorption at 77K.

Reactivity of the as-received fiber cloth in air at 573 K was very low; that is less than 1% weight loss in 10 hr and less than 4% weight loss in 70 hr. Reactivity of the HNO_3-oxidized sample D was still lower, that is 0.6% in 10 hr. Presumably this decrease in reactivity can be attributed to reduction in inorganic impurity content over that of the as-received cloth.

3.2. Ion Exchanged Fiber Cloth

In exploratory studies, potassium, sodium, calcium, and barium were exchanged onto the fiber cloth surface. As expected (3,18), they all catalyzed cloth reactivity to air at 573 K. However, for each cation, reactivity did not increase monotonically with increased loading; instead it went through a maximum. This would not be expected if the metal was added only by ion exchange (8). It was thought that some metal may have been derived from the metal acetate solution which was not completely removed from the cloth pore structure by washing. A more thorough study was performed using potassium, which is described herein,

*The latter finding is consistent with results of Deno who reports that a significant number of nitro groups are added to aromatic systems only when reacted with nitric acid at concentrations considerably in excess of the 54 wt% used in this study (14).

in an attempt to understand relations between cloth reactivity and how the metal was added.

In the first set of experiments, the cloth which had been oxidized using a cloth to HNO_3 ratio of 30 mg/cm^3 (Sample A) was exchanged in a potassium acetate solution (starting pH of 8.4) for 50 hr. The sample was then washed by refluxing in hot distilled water for varying lengths of time to remove potassium from the pore system. Figure 1 presents results for the amount of potassium remaining on the cloth as a function of washing time. It is clear that metal loading will be a function of not only the extents of oxidation in HNO_3 and subsequent cation exchange but also the severity of final washing. The curve in Figure 1 is characteristic of two concurrent processes of significantly different rates. It is suggested that the rapid process involves removal of the acetate from the pore system and the slow process involves back-ion exchange of hydrogen from hot water replacing potassium on the carboxyl groups. Extrapolation of the lower curve back to the ordinate yields a potassium concentration on the cloth at zero time of about 0.07%, which is taken as the maximum value of cation loading under the conditions of previous cloth oxidation and ion exchange used. It is concluded that following washing by refluxing for about 5 hr essentially all potassium derived from the acetate has been removed from the pore system and the potassium remaining is associated with carboxyl groups. For refluxing times progressively shorter than 5 hr, the contribution of potassium derived from the acetate to total potassium present increases sharply.

If we reason that the rate of back-ion exchange is more temperature dependent (that is, has a higher activation energy for its rate constant) than the rate of washing of the acetate from the pore system, then the use of cold water should separate the effects of these two processes still better than hot water. Thus washing of the cation exchanged cloth was also conducted in a continuous flow of fresh cold water (where an acetate ion concentration was not allowed to build up in the wash water as with refluxing). Following washing in cold water for 1 hr, the potassium concentration on the cloth was 0.078%, suggesting that essentially all acetate was washed out of the pore system but that little potassium cation associated with carboxyl groups had been removed.

Reactivity plots for the fiber cloth samples containing amounts of potassium varying from 0.006 to 0.265% are shown in Figure 2 for reaction times up to 8 hr. In some cases duplicate runs were made; in these cases data points give the average values and bars give the spread in values. Even though there is a monotonic increase in reactivity with increasing potassium loading, it is obvious that the specific activity of the catalyst decreases at higher loadings, as seen in Figure 3 where burn-off following reaction for 8 hr is plotted against potassium loading. This could be due to at least three reasons: (i) decreasing dispersion of the exchanged potassium with increasing concentration, (ii) poorer dispersion of the potassium derived from potassium acetate than that derived from the exchanged cation, and (iii) blockage of some of the pore system. Krypton surface areas of samples loaded to 0.133 and 0.265% potassium actually increased (1.9 m^2/g) over that of the oxidized fiber (1.0 m^2/g), and thus pore blockage at this level of loading was not present. The possibility that the degree of dispersion of the metal (or its oxide) is different following decomposition of the metal carboxylate which is bonded to the surface compared to decomposition of metal acetate particles (agglomerates) sitting on the surface is interesting to contemplate. A definitive answer does not come from this study, but is an important question when considering catalyst addition to carbon substrates and subsequent catalyst efficiency.

In additional experiments, cloths oxidized using cloth to HNO_3 ratios of 6.6 and 6.0 mg/cm^3 were exchanged with potassium acetate. For sample C, exchange was conducted for 30 hr, followed by washing for 1 hr using either refluxing in hot water or flowing cold water. Concentrations of potassium remaining in the fiber were 0.71 and 0.30 respectively. It is suggested, as just discussed, that the loading of 0.30% essentially represents potassium derived from carboxyl groups and that the loading of 0.71% represents potassium derived both from carboxyl and acetate entities. Enhanced loading from these two sources onto cloth sample C over that found on exchanged cloth sample A is consistent with the larger surface area (and pore volume) in the former sample.

The reactivity plot for the 0.30% potassium loaded sample is shown in Figure 4. Over the 8 hr period, reactivity continuously decreases with increasing reaction time despite a build-up in catalyst concentration in the carbon remaining. This suggests that: (i) increasing agglomeration (sintering) of catalyst particles is occurring with increasing burn-off, that is catalyst dispersion is decreasing and/or (ii) the catalyst is losing contact with the carbon surface. McKee and Chatterji have shown that the mechanism of catalysis of carbon gasification by potassium involves oxidation-reduction steps (19). That is, the higher oxide K_2O_2 is reduced by the carbon to K_2O which, in turn, is reoxidized to K_2O_2 by air. The rate of agglomeration is dependent upon the mobility of the catalyst species on the surface. Even though reaction temperature was below the melting point of K_2O_2 (663 K), Thomas and Walker (20) have shown that solid catalyst particles can have high mobility on carbon surfaces, particularly in an oxygen environment. Further, Baker has shown, from in-situ electron microscopy studies, that species on carbon surfaces in an O_2 atmosphere commence having significant mobility above their Tammann temperature, that is one half their melting temperature, expressed in degrees K (21). Thus, at a reaction temperature of 573 K, K_2O_2 (having a Tammann temperature of 332 K) would be expected to have significant mobility on carbon surfaces.

Burn-offs in 8 hr for the samples loaded to 0.30 and 0.71% potassium are given in Figure 3. As with cloth sample A, it is suggested that there is an optimum potassium loading to achieve maximum cloth reactivity for Sample C. Additional loading increases reactivity only slightly or may, in some cases, even decrease reactivity, as will now be seen.

For Sample D, exchange was conducted for 10, 30, and 50 hr in potassium acetate followed by washing in running cold water for 1 hr. Loadings of potassium were 0.52, 0.79, and 1.8%, respectively. These results suggest that transport of the acetate solution into and out of the fiber cloth pore system was slow This is consistent with this oxidized sample having some molecular sieve character, as previously discussed. Figure 4 presents reactivity plots for the samples loaded to 0.52 and 0.79% potassium. Again reactivities decrease continually with increasing time of reaction. Burn-offs in 8 hr for all samples are given in Figure 3. For sample D, again an optimum potassium loading is suggested; at higher loadings there is a significant decrease in cloth reactivity, probably due to pore blockage and/or coverage of the carbon surface with more than a monolayer of potassium. That is, washing the sample, which was exchanged for 50 hr, in running cold water for 1 hr appears to have not removed all potassium acetate from the pore system. If optimum loading is taken as about 0.79% potassium and if it is assumed that each potassium atom was previously associated with a carboxyl group, it is calculated that the potassium carboxylate occupied about 10 m^2/g of surface. Again this is larger than the Kr area of oxidized

cloth sample D and is consistent with molecular sieving. However, the area is much less than that which was estimated to be occupied by carboxyl groups following nitric acid oxidation (that is, 195 m^2/g). This suggests that: (i) potassium only exchanged on a small fraction of the carboxyl groups following oxidation, (ii) oxidation in nitric acid added both carboxyl, acidic phenolic and lactone groups to the fiber surface, and/or (iii) nitric acid was not completely washed from the pore system.

4. CONCLUSIONS

The reactivity of PAN fiber cloth to air can be substantially increased by the addition of metals to the cloth via ion exchange from metal acetate solutions. However, since the surface area of PAN fibers (even those heated to less than 1800 K) is very low, significant metal addition via ion exchange can only be achieved if the fiber is first treated with nitric acid to increase surface area and, as importantly, to add carboxyl groups. The amount of metal which can be added to the fiber is a function of the severity of oxidative treatment, the time of subsequent exchange, and the degree of subsequent removal of metal from the fiber by washing. Fiber cloth reactivity to air appears to increase essentially linearly with increase in potassium loading via ion exchange. Additional potassium loading originating from potassium acetate left in the pore system of the fibers following washing appears to increase reactivity only slightly in some cases and in other cases to, in fact, result in reduction in fiber cloth reactivity. It is suspected that there will be an optimum in the extent of fiber oxidation to achieve enhanced reactivity. At the optimum, both fiber cloth reactivity and mechanical properties of composites made therefrom will be enhanced. Too much fiber oxidation will lead to an unacceptable reduction in mechanical properties of the composites subsequently fabricated, even though fiber reactivity to air may be further enhanced.

5. RECOMMENDATIONS

Etching of carbon fibers in nitric acid in order to introduce additional open porosity has been found by other workers to increase the shear modulus of fiber-polymer composites (4). The increase has been attributed to enhanced bonding area between the fiber surface and resin matrix. We have now shown that fiber reactivity to air can be enhanced by following nitric acid etching (oxidation) of PAN fibers with addition of metals to the fiber surface by ion exchange. It is recommended that research be started to study the effect of the association of metal cations with carboxyl groups on the fiber surface on polymerization of the monomer in composite fabrication and on the subsequent values of tensile strength, Young's modulus, and shear modulus of the composites produced. Optimization of the system is felt to be of importance.

6. NEW TECHNOLOGY

New technology in this research involves the oxidation of carbon fiber cloth in nitric acid solution followed by the addition of metal cations to the cloth by ion exchange with hydrogen on the carboxyl groups using the appropriate metal acetate solution. Such treatment can markedly enhance the reactivity of carbon fiber cloth to air, the extent of reactivity increase depending on the amount of metal cation added to the fiber cloth by ion exchange.

The innovators of this process are: T. A. Eapen, I. M. Ismail, O. P. Mahajan, and P. L. Walker, Jr.

Information on the process was reported in informal reports submitted to JPL, dated April 17, 1979 and August 1, 1979. In the April 17 report, a description of the new technology was covered on pp. 2, 3, 5 - 8, and Figures 8 and 9. In the August 1 report, a description of the new technology was covered on pp. 1 - 3 and Figures 1 - 4.

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Table 1

SELECTED PROPERTIES OF FIBERS IN T-300 CARBON CLOTH

Surface Area, m^2/g	0.37
L_c, nm	1.1
Interlayer spacing, nm	0.356
Hg density, g/cm^3	1.71
X-ray density, g/cm^3	~2.14
He density, g/cm^3	1.79
Total Porosity, cm^3/g	0.117
Open Porosity, cm^3/g	0.026
Closed Porosity, cm^3/g	0.091

Table 2

INORGANIC ELEMENTS PRESENT IN T-300 FIBER CLOTH

Element	Amount, wt%
Na	0.2
K	0.015
Ca	0.03
Ba	0.003
Fe	0.02
Mg	0.004
Zn	0.01
Ti	0.003
Al	0.01
Si	0.03

Not detected: B, Sb, Pb, Ge, In, Bi, V, Ni, Co, Be, Sr, Ce, La, Zr, Y, Mn, Cr, Ag, Cd, Sn.

Table 3

SURFACE AREA DEVELOPMENT IN T-300 FIBER CLOTH UPON HNO_3 OXIDATION

Sample	Cloth to Acid mg/cc	Surface Area m^2/g
A	30	1.0
B	25	1.2
C	6.6	1.5
D	6.0	2.3

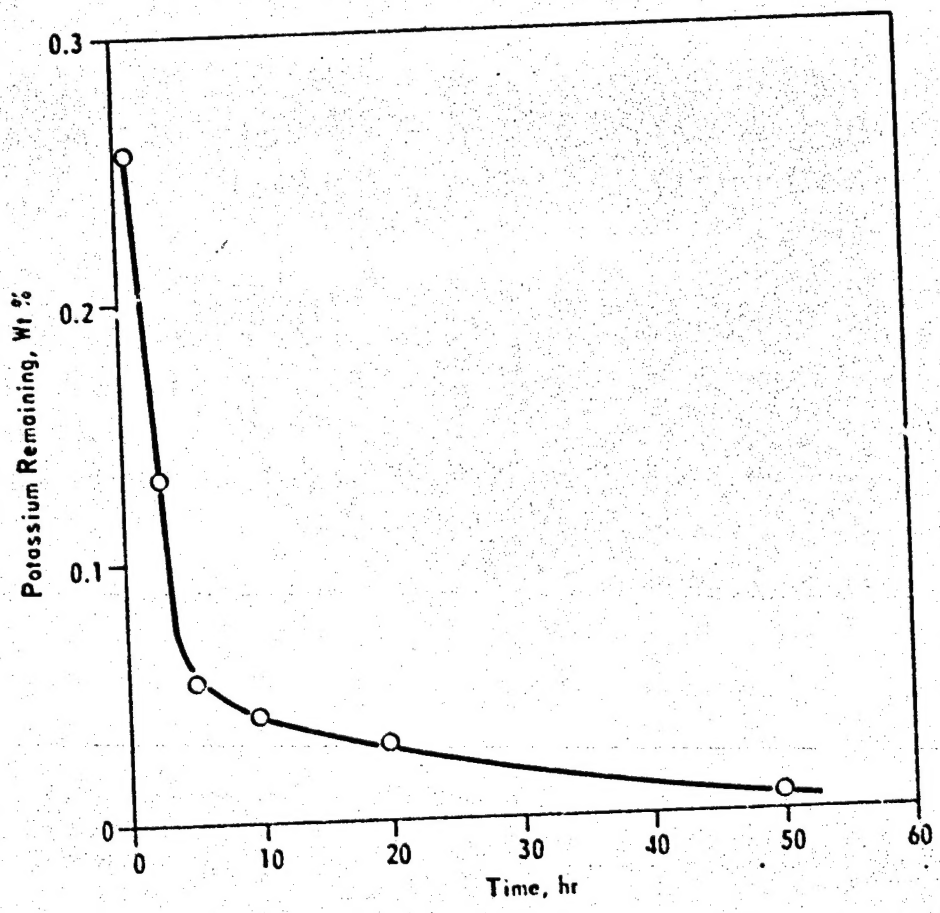

Figure 1. EFFECT OF TIME OF WASHING BY REFLUXING IN HOT WATER ON POTASSIUM CONTENT IN CLOTH SAMPLE A
Sample A previously exchanged with potassium acetate for 50 hr

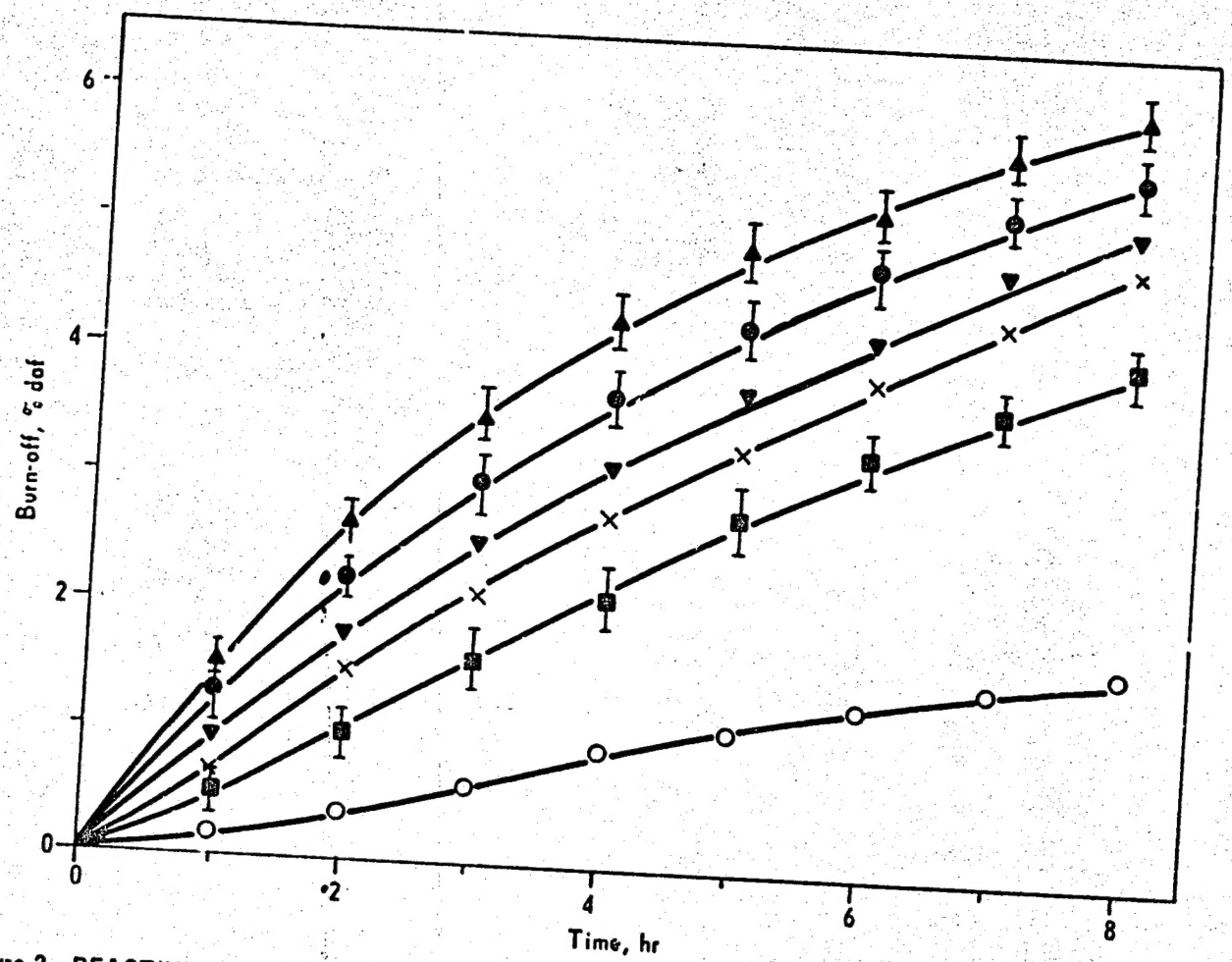

Figure 2. REACTIVITY PLOTS OF CLOTH SAMPLE A IN AIR AT 573 K FOR VARIOUS POTASSIUM LOADINGS, IN WT %: ○ 0.006; ■ 0.031; × 0.045; ▼ 0.051; ● 0.133; ▲ 0.265

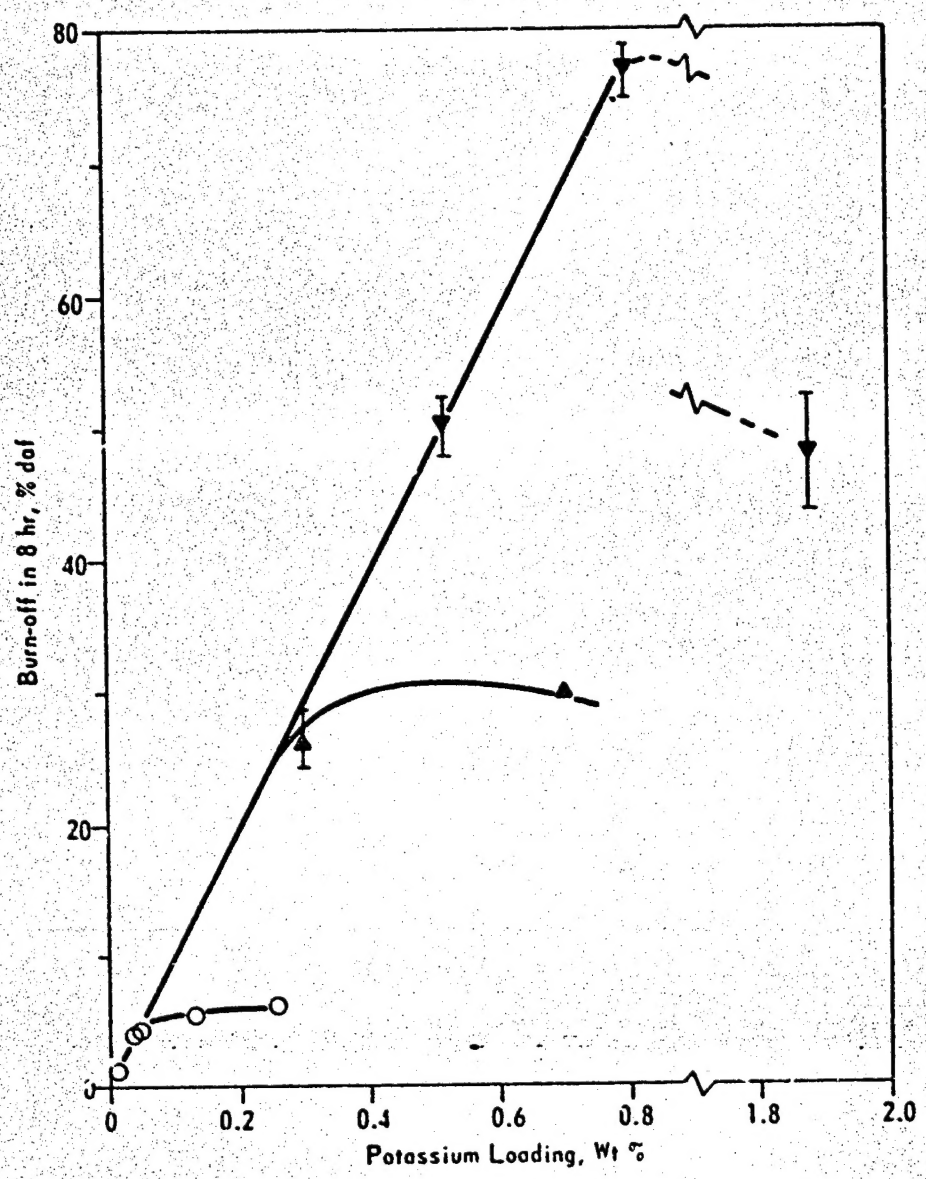

Figure 3. EXTENT OF BURN OFF IN 8 HR IN AIR AT 573 K OF CLOTH SAMPLES LOADED WITH VARYING AMOUNTS OF POTASSIUM
Sample: ○ A; ▲ C; ▼ D.

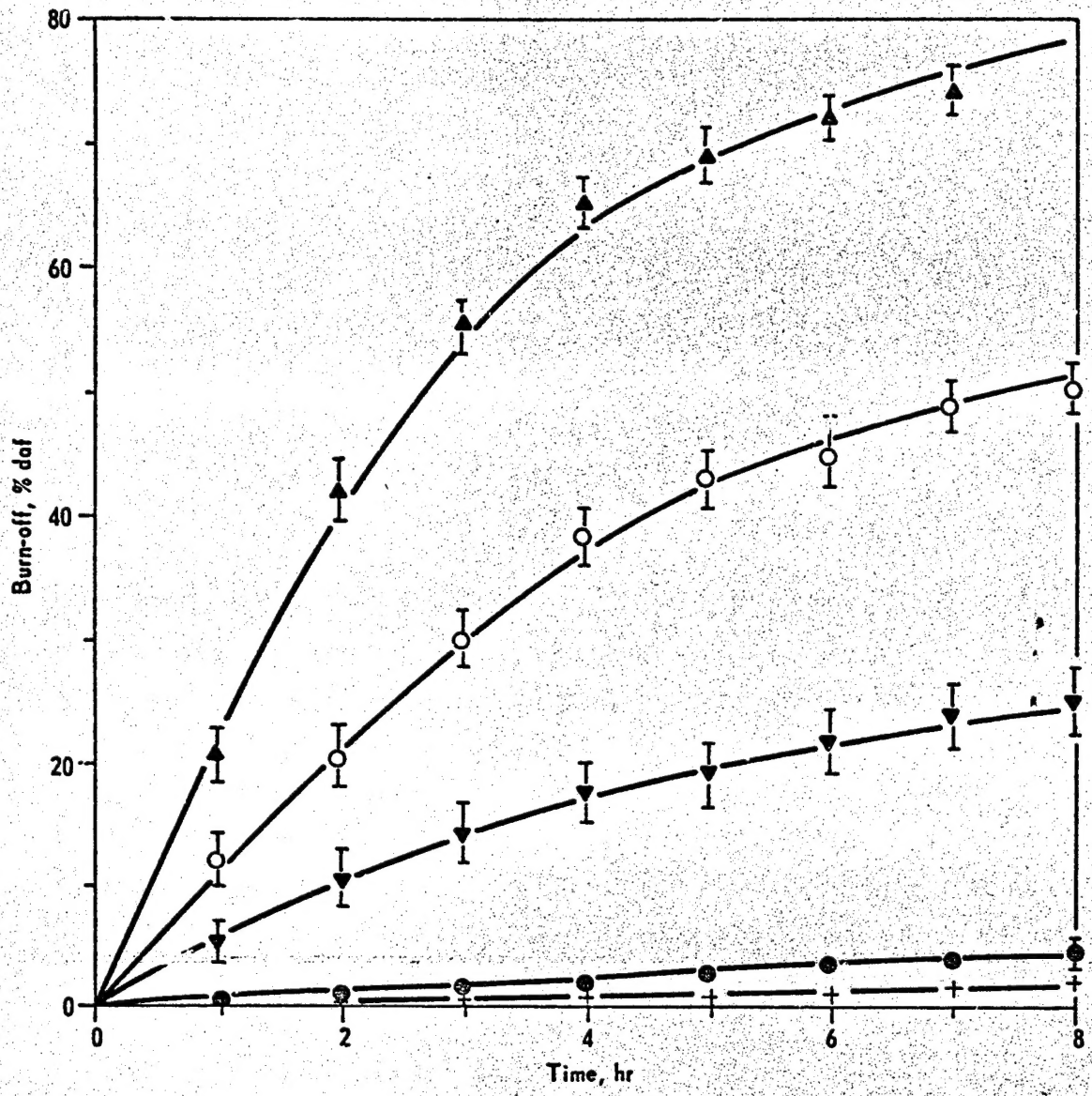

Figure 4. REACTIVITY PLOTS OF CLOTH SAMPLES WITH VARIOUS POTASSIUM LOADINGS IN AIR AT 573 K.
Sample: + A–0.006% K; ● A–0.031% K; ▼ C–0.30% K; ○ D–0.52% K; ▲ D–0.79% K.

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